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AN IMPORTANT ANNOUNCEMENT

ANNUAL CONVENTION OF CHEMISTS, 1978

The Annual Convention of Chemists 1978 will be held at Waltair from 27 to 31st December 1978 instead of 25th to 28th December 1978 at the Andh University, Waltair-530 003.

Executive Secretary
Indian Chemical Society,
Calcutta-700 009.

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Reactions of Metal Alkoxides with β-Diketones and β-Ketoesters*

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A. INTRODUCTION

1. *History :*

METAL β-diketonates are amongst the most widely studied coordination compounds and their chemistry has been investigated for almost all metals and metalloids in the periodic table. The coordination tendency of β-diketones is now well established and a large number of more potential ligands, being synthesised by organic chemists every year, are used to prepare new complexes with metals to elucidate with greater clarity the nature of bonding, etc. and to develop newer applications of the same.

The chemistry of metal β-diketonates in a sense reflects the different eras in the development of inorganic chemistry as a whole[1]. Starting with the synthesis of these derivatives for the first time in 1887 by Combes[2], the nature of bonding was elucidated by the classical work of Werner[3] in 1890's, followed later by studies by Morgan[4] and Sidgwick[5] in 1920's and their coworkers who drew attention to the predominant chelating character of these ligands. A new dimension was added to the understanding about the nature of bonding in these derivatives by Calvin and Wilson[6], who in 1945 suggested the presence of aromaticity in β-diketonate rings ; this aspect of work has been later pursued by Collman[7] and others. With increasing applications of sophisticated instrumental techniques for the structural determination, the classical work of Cotton and Holm[8] in 1958 on trimeric nickel *bis*(acetylacetonate) opened a new chapter in this field. The work of Lewis and coworkers[9] during sixties has further demonstrated a new type of bonding mode of these ligands with some metals like platinum etc. A new chapter in the field of a closely allied series of derivatives was introduced in 1969 by Chaston and Livingstone[10] who investigated a series of metal thio-β-diketonates by replacing carbonyl oxygens of β-diketones with sulfur atoms. Since then, a large number of metal monothio- and dithio-β-diketonates have been synthesised and their properties have been studied.

Apart from the theoretical importance of the topic, multifarious practical applications in analytical operations and other industrial uses have led to a rapid development in the field of metal β-diketonates, which can be discerned by the publication of more than 1500 papers during the last two decades on different aspects of the chemistry of these complexes.

II. *Classification of metal β-diketonates :*

Metal β-diketonates may be classified into following three categories depending upon the mode of bonding of ligand moieties with metal atoms :

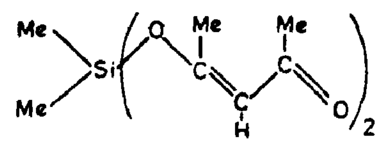
(i) Oxygen bonded β-diketonato complexes,

(ii) Carbon bonded β-diketonato complexes,

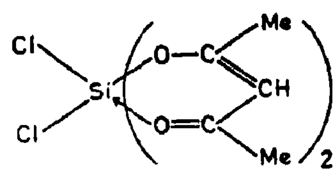
(iii) Both Carbon and Oxygen bonded β-diketonato complexes.

(i) *Oxygen bonded β-diketonato complexes*

In these derivatives, β-ketoenolate anion acts as an unidentate ligand, e. g. in $Me_2Si(acac)_2$,

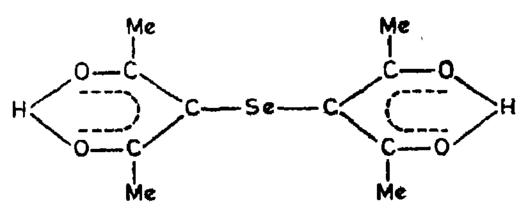


or as bidantate ligand which is the usual mode of bonding of β-diketones with most of the metals of the periodic table, e.g., $Cl_2Si(acac)_2$:



(ii) *Carbon bonded β-diketonato complexes*

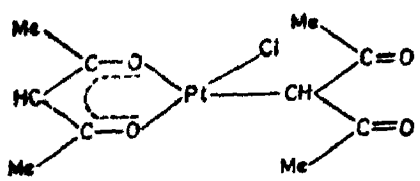
In β-diketonato complexes of sulphur, selenium, tellurium, mercury, platinum and gold, the ligand carbonyl groups do not appear to participate in bonding, e.g., $Se(acac)_2$ may be repesented as



(iii) *Both Carbon and Oxygen bonded β-diketonato complexes*

In some β-diketonate complexes of platinum, e.g., $PtCl(acac)_2$, one of the ligand moieties is bonded to platinum via both carbonyl oxygen atoms while the other moiety is bonded through the 3-carbon atom only :

* Presidential address of the Indian Chemical Society for 1977 delivered on December 26, 1977 at Jaipur.



These stable complexes are generally coloured and soluble in common organic solvents.

III. Uses :

The tendency of these β-diketone ligands to form *inner coordination* compounds with a variety of metals provided the inorganic chemists with a large number of derivatives which at one time could be considered as rare examples of electropositive metals in combinations depicting the characteristics of covalent compounds, i.e., volatility and solubility in organic solvents. These special characteristics of metal β-diketonates have been used in solvent extraction studies of various metal ions. Exceptional volatility of derivatives with fluorinated β-diketones has been exploited increasingly in gas chromatographic separations of metals.

A novel application of some lanthanide β-diketonates in structural elucidation of organic compounds by P. M. R. technique was discovered by Hinckley[11] for the first time in 1969. Since then, a wide variety of applications have been described for these complexes, termed under the general name of 'lanthanide shift reagents'[12]. The application of $Cr(acac)_3$ has recently been shown by Gansow *et.al.*[13] in a better resolution of C-13 N.M.R. spectra also of some metal carbonyls.

Since the first publication by Lempicki and Samelson[14] on their laser activity, considerable work has been carried out on such properties of β-diketonates, particularly of europium.

B. A Brief Resume of Work carried out in our Laboratories

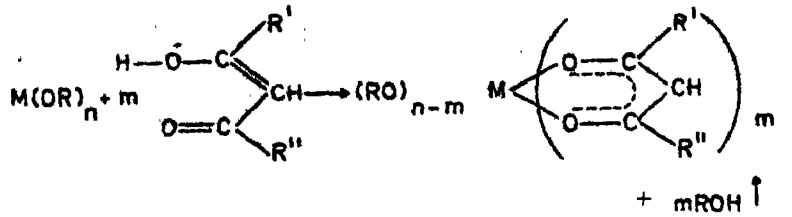
1. Reactions of metal alkoxides with β-diketones and β-ketoesters :

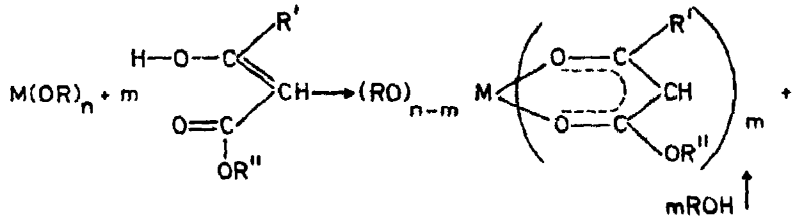
The marked reactivity of metal alkoxides towards any organic reagent having a hydroxy group led us to look into the reactions of metal alkoxides on the β-diketones, β-ketoesters and allied reagents. As most of this work was carried out in the laboratories of the University of Rajasthan, where this annual meeting of the Indian Chemical Society is being held, I thought it appropriate to describe the same briefly on this occasion. A large number of novel derivatives with metals depicting uncommon coordination numbers have been synthesised during the course of this work, but it has not been possible to elucidate or confirm their structural details fully due to lack of sophisticated physico-chemical techniques; the present account, I hope, would, therefore, indicate a rich field of research for further structural determination by coordination chemists.

As indicated above, metal alkoxides depict marked reactivity towards any reagent with a hydroxy group. The β-diketones as well as β-ketoesters are well known to show tautomerism, the enol form of which generally has a hydroxy group available for reaction. These reagents, therefore, depict a very facile reactivity towards metal alkoxides, in which the alkoxy group is replaced by the enolate form of the β-diketonate or β-ketoester reagent. The reactions of titanium alkoxides with β-diketones and β-ketoester in 1 : 1 and 1 : 2 molar ratios were investigated by Schmidt[15] and the *mono*- and *bis*-derivatives thus isolated were both assigned hexacoordinated structures which were later supported by cryoscopic molecular weight study[16]. Contrary to the above, Yamamoto and Kambara[17] assumed 5- and 6-coordinated structures for the *mono*- and *bis*-derivatives respectively on the basis of infra-red studies. These workers did not observe any replacement beyond the formation of *bis-derivatives* ; the hydrolysis of *bis*-derivative led to the formation of *titanyl bis*(acetylacetonate). Mehrotra and coworkers[18-21] studied in detail the reactions of titanium alkoxides with β-diketones, fluoro-β-diketones, and β-ketoesters in 1 : 1 and 1 : 2 molar ratios and *mono*- as well as *bis*-chelates were obtained, respectively. In order to explore the possibility of further replacement, a reaction of dialkoxide *bis*(acetylacetonate) with excess of acetylacetone was carried out and it was observed that the reaction was quite slow, yet the third alkoxy group was replaced, but the *tris*(acetylacetonate) derivative thus formed decomposed instantaneously to give titanyl *bis*(acetylacetonate). Compared to the non-volatile nature of β-diketonates, the corresponding fluoro-β-diketonates of titanium are more volatile products and could be distilled *in vacuo*.

Fay *et.al.*[22,23] have assigned the *trans*-configuration for hexacoordinated *bis*(acetylacetonate) derivatives of titanium. Nevertheless Bradley and Holloway[24,25] on the basis of P.M.R. studies on these derivatives ruled out the possibility of *trans*-configuration in favour of *cis*-configuration. These workers found that all the products of type $Ti(acac)_2X_2$ exist only in *cis* form (optically active) over a wide temperature range. Activation energies for intramolecular exchange of ligands in these functional molecules showed that steric hindrance of the alkoxy group increased the energy of activation, but did not promote the formation of the *trans* form.

Following the investigations with titanium alkoxides, the reactions of a large number of metal alkoxides (generally ethoxides or *iso*propoxides) with β-diketones and β-ketoesters have been carried out in our laboratories. These reactions can be represented by the following general equations :

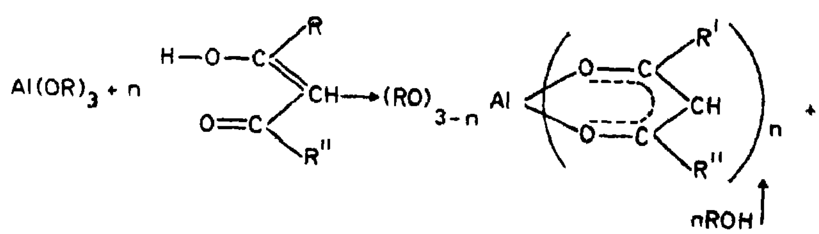




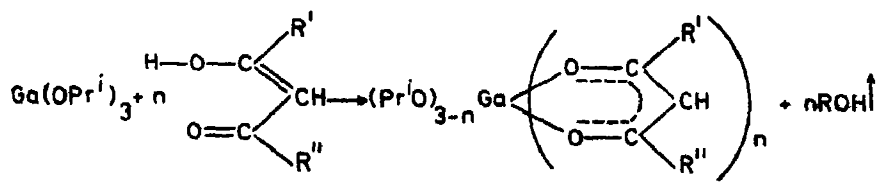
(R = Et and Pr^i)

In general, the metal alkoxide is mixed with a stoichiometric amount of the desired ligand in benzene medium and after fractionation of the benzene-alcohol azeotrope, the corresponding β-diketonate or β-ketoester derivative can be isolated by removal of excess benzene by evaporation[26]. The advantage of this method is that the complexes having different apparent coordination numbers can be readily synthesised using the desired stoichiometric ratio of the ligand.

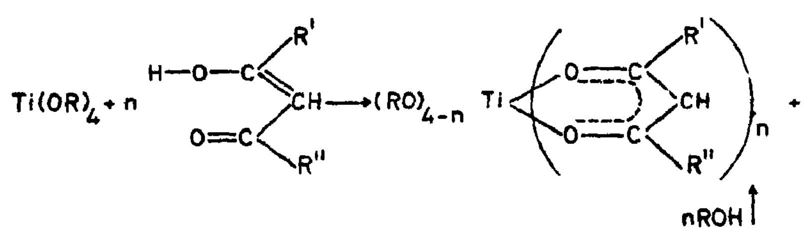
In the following paragraphs is being described a brief summary of the reactions studied in our laboratory, in the form of general equations, indicating the formation of metal chelates of varying coordination numbers employing different stoichiometric ratios of the reactants :



(R = Et, Pr^i ; R′ = R″ = CH_3 ; R′ = CH_3, R′ = C_6H_5 ; R′ = CH_3, R″ = OC_2H_5 , n = 1-3)[17].



(R′ = R″ = CH_3*; R′ = CH_3, R″ = OCH_3 ; R′ = CH_3, R″ = OC_2H_5 ; n = 1–3)[18].

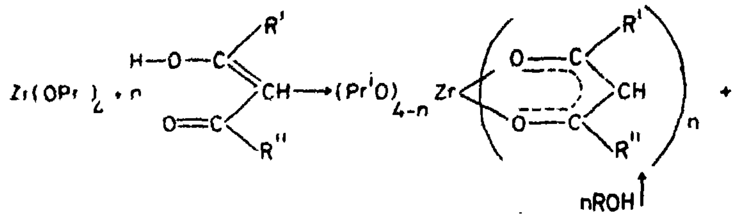


(R = Et, Pr^i ; n = 1, 2 ; R′ = R″ = CH_3 ; R′ = CH_3, R″ = C_6H_5 ; R′ = R″ = CF_3, R′ = CF_3, R″ = C_6F_5 ; R′ = CH_3, R″ = OCH_3 ; R′ = CH_3, R″ = OC_2H_5)[19-21].

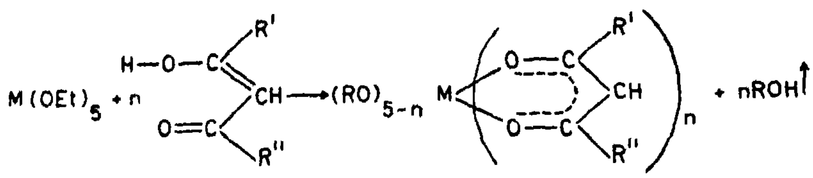
$$(OR)_2Ti(OCCH_3CHCOCH_3)_2 + CH_3COCH_2COCH_3 \longrightarrow ROH + (RO)Ti(OCCH_3CHCOCH_3)_3$$

$$\downarrow \text{decomposed}$$

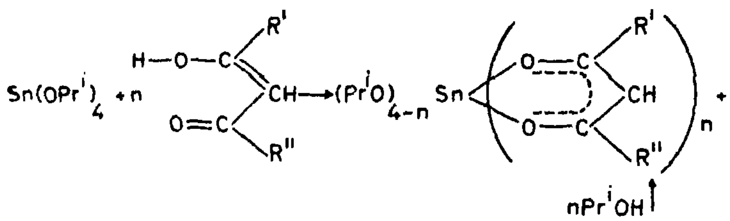
$$CH_3C(OR)CHCOCH_3 + O{=}Ti(OCCH_3CHCOCH_3)_2$$



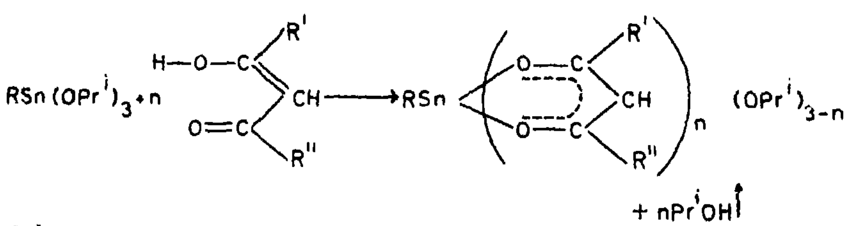
($R'=R''=CH_3$, $R'=R''=CF_3$, $R'=CH_3$, $R''=C_6H_5$; $R'=CH_3$, $R''=OCH_3$; $n=1-4$)[29,30].



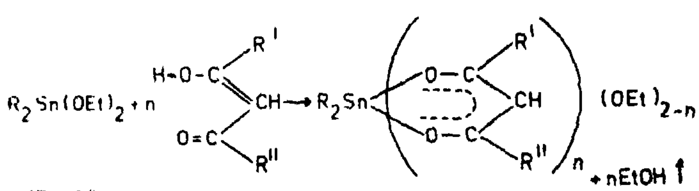
($M=Nb, Ta$, $n=1-3$; $R'=R''=CH_3$; $R'=CH_3$, $R''=C_6H_5$; $R'=R''=C_6H_5$; $R'=CH_3$; $R''=OCH_3$, $R'=CH_3$, $R''=OC_2H_5$)[31-34].



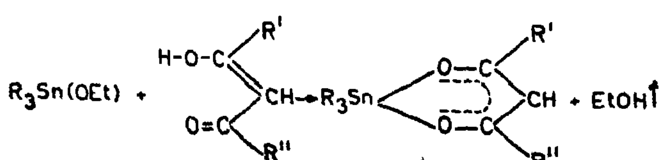
($R'=R''=CH_3$; $R'CH_3$, $R''=C_6H_5$, $R'=R''=C_6H_5$; $n=1, 2$)[35].



($R=Et, Bu^n$, $n=1,2$ when $R'=CH_3$, $R''=C_6H_5$ and $R'=R''=C_6H_5$; $n=1-3$ when $R'=R''=CH_3$)[36].



($R'=R''=CH_3$, $R'=CH_3$, $R''=C_6H_5$, $R'=CH_3$, $R''=OCH_3$; $n=, 2$)[37]



($R'=R''=CH_3$; $R'=CH_3$, $R''=C_6H_5$; $R'=CH_3$, $R''=OCH_3$)[37].

4

II. Some Salient Results from this work :

For the benefit of my younger friends continuing to struggle in ill-equipped laboratories even now, I would crave your indulgence in pointing out that with the penetrating insight of my young students and coworkers, we could, during the course of these investigations, correct some long standing errors which had crept even in undergraduate textbooks on the supposed trimeric structure of titanium as well as tin dichloride *bis*(acetylacetonate) and we were also successful in the synthesis of anhydrous β-diketonates of lanthanide elements, for which quite a few unsuccessful and doubtful efforts had been published in the literature earlier.

Our first publication in the field of mixed metal alkoxide β-diketonates was on the synthesis of titanium diethoxide *bis*(acetylacetonate) which was found to be monomeric in a number of organic solvents[38]. This led us to some doubts on the reported molecular complexity of titanium dichloride *bis*-(acetylacetonate), synthesised in the beginning of this century independently by Rosenheim[39] and Dilthey[40]. This product was assigned an ionic structure of type $[Ti(acac)_3]_2^+ [TiCl_6]^{-2}$, which is the trimeric form of $TiCl_2(acac)_2$ merely on the basis of analogy with the product $Si(acac)_3Cl.HCl$ and $Zr(acac)_3Cl$, obtained earlier in the corresponding reactions of acetylacetone with silicon or zirconium tetrachlorides. The only evidence adduced in support of the above structure was that the product on treatment with ferric chloride gave a product of the composition $[Ti(acac)_3].[FeCl_4]$, the formation of which could be easily explained on the basis of the following plausible reaction :

$$[Ti(acac)_3]_2^+ [TiCl_6]^{-2} + 2FeCl_3 \rightarrow 2[Ti(acac)_3] [FeCl_4] + TiCl_4.$$

On repeating the experimental work of Rosenheim and Dilthey, the analytical results of the products obtained did correspond to $Ti(acac)_2Cl_2$ and $[Ti(acac)_3]$ $[FeCl_4]$. However, on actual measurements of the molecular weights of the derivative $Ti(acac)_2Cl_2$ in a number of common organic solvents, the observed experimental value was found to correspond to the simple monomeric $Ti(acac)_2Cl_2$. Further the derivative was found form, to be a non-electrolyte in these solvents, thereby ruling out the possibility of the above trimeric formation $[Ti(acac)_3]_2^+.[TiCl_6]^{-2}$, as suggested earlier.

The product of the reaction between titanium tetrachloride and excess of acetylacetone was, thus, shown to be a simple hexa-coordinated derivative $TiCl_2(acac)_2$. This was also in conformity with a considerable amount of work on the reactions of titanium tetrachloride with reagents having active hydroxy groups like alcohols[41], and carboxylic acids[42] in which two of the four chlorine atoms on titanium tetrachloride were shown to be much more reactive.

The formation of the product $[Ti(acac)_3].[FeCl_4]$ from the reaction of $TiCl_2(acac)_2$ and $FeCl_3$ has been shown to be much more complica ted and efforts have been made to elucidate it in a number of publications[38,43,44].

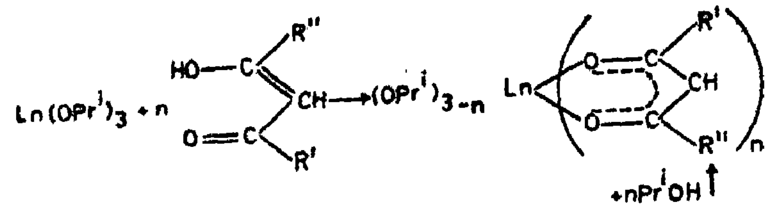
In the reaction of stannic chloride with acetylacetone in chloroform at room temperature, we isolated a product of composition $SnCl_4$. acacH which was found to be stable even upto 60-70° under 0.1 mm pressure, but decomposed above 90-100° to give stannic dichloride *bis*(acetylacetonate) as follows[45] :

$$2SnCl_4.Hacac \rightarrow SnCl_2(acac)_2 + SnCl_4 + 2HCl$$

Stannic dichloride *bis*(acetylacetonate) has been prepared alternatively by refluxing stannic chloride and acetylacetone in benzene or chloroform and it also been shown to be a monomeric covalent compound[46].

In still another field, the simple technique of the reactions of metal alkoxides with β-diketones and β-ketoesters appears to have provided a very convenient route for the preparation of anhydrous lanthanide derivatives for the first time in 1965. Earlier methods used for the preparation of lanthanide *tris*-β-diketonates were examined critically by Pope *et. al*[47]. and by Moeller *et. al*[48]. who have conclusively established that the products from aqueous solutions were invariably hydrates, from which generally hydroxy derivatives were obtained on dehydration even under mild conditions- Attempts have been made to synthesize these deri. vatives in non-aqueous media also by (*i*) the reaction of lanthanon metal with excess acetylacetone using metal evaporation technique[49] or (ii) by the reaction of lanthanide hydrides[50,51] with excess acetylacetone in the presence of acetic acid. Lis and Bos[52] have very recently claimed to have isolated a crystalline *tris*-chelate by the former method, yet according to their own description, unusual properties like large number of extra peaks in infra-red spectra, low m. p. (94°) and observed loss in weight when the derivatives are exposed to air, probably indicate the presence of same volatile fractions in their products which might have been formed in the side-decomposition reactions earlier.

Employing lanthanide alkoxides as the starting materials, we have been able to synthesise in our laboratory in 1965, pure *tris*-acetylacetonates of lanthanum[53], praseodymium[54] and neodymium[55]. The lanthanide *iso*propoxides interchange their *iso*-propoxy groups with β-diketones and β-ketoesters in different molar ratios to yield mixed as well as *tris*-chelates :



($Ln = La^{3+}, Pr^{3+}, Gd^{3+}, Er^{3+}, Y^{3+}, Yb^{3+}$; $R' = R'' = CH_3$; $R' = CH_3, R'' = C_6H_5$; $R' = R'' = C_6H_5$; $R' = CH_3$, $R'' = OCH_3$; $R' = CH_3$, $R'' = OC_2H_5$; n = 1, 2)

These *tris*-β-diketonates have been shown to be dimeric products, which are not as highly hygroscopic as the products claimed earlier as anhydrous *tris*-derivatives. A plausible explanation of this has been offered recently by the author.[57]

For example, the dihydrates $Y(acac)_3 \cdot (OH_2)_2$ and $La(acac)_3 \cdot (OH_2)_2$ have been shown[58,59] to depict an octa-coordinate positions on the square face of the antiprism :

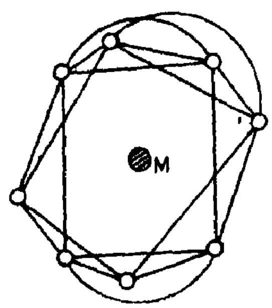


Fig. 1. Structure of Ln $(acac)_3(OH_2)_2$ unit.

Mere removal of the two water molecules under as mild conditions as possible to avoid hydrolysis would probably leave an open unaltered structure with two coordination sites vacant. This explains the extremely hygroscopic nature of such dehydrated products as to make their handling even for any physico-chemical measurements very difficult without rehydration. It may be interesting that the anhydrous dimeric products obtained in our laboratories through the alkoxides are fairly stable to atmospheric structure and one of the plausible structures which can be assigned to them could be of the type[51] shown in Fig. 2 in which two square anti-prisms share one square face :

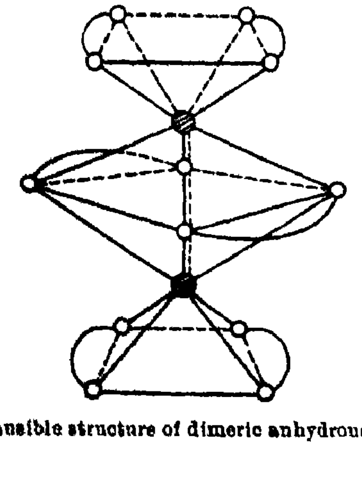


Fig. 2. A plausible structure of dimeric anhydrous $[Ln(acac)_3]_2$.

C. Acknowledgements

Before I close, it is my pleasant duty to thank all the younger co-workers and colleagues whose work has been presented by me in this presidential address.

Let me also take advantage of this opportunity of conveying my grateful thanks to all the fellow chemists who did me the great honour of electing me the President of our Indian Chemical Society. I am also thankful to all the fellows, office-bearers and the administrative staff of the Society for the cooperation which I received in the discharge of my duties as the President of the Society.

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Alkali Metal Complexes : Mixed Ligand Complexes of Alkali Metal Salts of Some Organic Acids with Oxygen Donor Ligand—Isatin.

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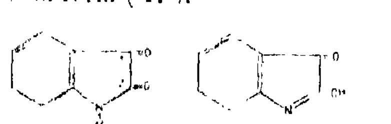
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Isatin (indole-2, 3-dione) shows lactam and lactim structures and in the solid state lactam variety predominates. Mixed ligand complexes of isatin and metal salts of organic acids (glycine, β-alanine, isonitrosoacetophenone, 1-nitroso-2-naphthol, α-picolinic acid, o-nitrophenol and 8-hydroxyquinoline) of Li, Na and K have been synthesised and their structures investigated, with particular regard to the co-ordination sites.

And by comparing the donor properties of isatin and its two methyl derivatives (N—methylisatin and O—methylisatin), it has been found that in these alkali metal adducts, isatin retains the lactam structure.

ONE of the most fascinating features of chemistry of 'tautomeric ligands' is the variety of ways in which their *keto-enol* (or lactam-lactim) anions can bond to metallic atoms to give varied molecular structures ; and we are extending our studies with oxygen and nitrogen donor ligands which exhibit preferential *keto-enol* structure while co-ordinating with different alkali metals, under different conditions.

Isatin (indole-2,3-dione) shows lactam and lactim structures, and in the solid state lactam variety predominates. Isatin presents one of the oldest of tautomerism, and reacts in the lactam form (I) or lactim form (II).



In the present work, mixed ligand complexes of isatin and metal salts of organic acids (glycine, β-alanine, isonitrosoacetophenone, 1-nitroso-2-naphthol, picolinic acid, o-nitrophenol and 8-hydroxyquinoline) of lithium, sodium and potassium have been synthesised and their structures investigated with particular regard to their co-ordination sites.

Results and Discussion

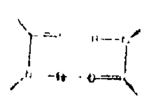
Our usual method of preparation was to make a concentrated solution of the alkali metal salts in absolute ethanol and add to it the second ligand-isatin. The mixture was warmed and on cooling the adducts separated of the general formula ML.*n*. Isatin, where HL = the organic acids, M = Li, Na and K ; the number of isatin molecule in the adducts has always been one (n = 1).

All the complexes of isatin are coloured crystalline compounds. These complexes are slightly soluble in most polar solvents, but are insoluble in non-polar solvents. These complexes are rapidly hydrolysed by exposure to moisture, but are stable when kept in vacuo or in dry, oxygen-free atmosphere.

No conclusion can be drawn from examining the action of heat on complexes which appear to either decompose or undergo a transformation at a temperature slightly lower than the melting point of the second ligand (isatin). The analysis and physical properties of these complexes are given in the Table 1.

The infra-red spectra of all the compounds heve been measured in the region 4000-650 cm^{-1} in Nujol mulls. The selected absorption bands are given in Table 2.

In cyclic lactams the N – H frequency is at 3440 cm^{-1} when free and 3175 cm^{-1} (dimeric structure) when associated. The N – H stretching frequency of isatin just like cyclic lactams, show a broad absorption at 3180 cm^{-1}, suggesting association and a dimeric lactam structure.



That these adducts are not simple physical mixtures of the two components is shown by examining the infra-red spectra, which differ markedly from a physical mixture of the two components. All these adducts have bands between 2600-3150 cm^{-1}, which are missing in both the components with the exception of K.1N2N.Isatin and K.INAP.Isatin, where the band is at 3180 cm^{-1}. The N – H band in M.8HQ.Isatin complexes, is shifted down to 3140 cm^{-1} in case of Li, 3120cm^{-1} for Na and 3070 cm^{-1} for K ; while for the rest of the complexes, the band is shifted down to the region 2620-2710 cm^{-1}. These bands could be assigned to a N – H...O absorption, which would account for the absence of N – H absorption above

TABLE—1

SOME PROPERTIES AND ANALYTICAL DATA

Compound	Colour	Transition temp. or Decomposition temp. (°C)	Found (%)				Calculated (%)			
			C	H	N	M	C	H	N	M
Li8 HQ.Isatin	Yellow	245 d	67.31	4.49	8.85		68.45	3.69	9.39	
Na8 HQ. Isatin	Yellow	200 d	63.65	3.82	8.22	6.85	64.93	3.50	8.51	7.31
K 8 HQ. Isatin	Pale yellow	170 d	59.92	4.80	8.25	11.60	61.81	3.33	8.48	11.81
K1N2N. Isatin	Dark brown	155 d	61.30	4.54	7.42	10.15	60.33	3.07	7.54	10.39
KONP. Isatin	Yellowish brown	160 d	52.31	3.41	8.40	11.65	51.85	2.74	8.83	12.03
NaPicA. Isatin	Deep yellow	160 d	56.83	4.02	9.20	9.10	57.53	3.08	9.58	9.67
K PicaA. Isatin	Yellow	140 t	55.02	3.85	8.78	11.80	54.54	2.92	9.09	12.33
NAGly. Isatin	Deep pink	215 d	50.25	4.31	10.78	8.75	49.18	3.68	11.06	9.42
K Gly. Isatin	Deep pink	210 d	45.30	4.15	10.48	14.25	46.15	3.46	10.76	15.00
LiAln. Isatin	Yellowish green	98 d	52.89	4.79	11.25		54.54	4.54	11.57	
NaAln. Isatin	Yellowish green	93 d	50.20	4.85	10.52	8.20	51.16	4.26	10.71	8.91
K Aln. Isatin	Yellowish green	90 d	46.97	4.66	9.98	13.65	48.17	4.01	10.20	14.28
NaINAP.Isatin	Reddish brown	130 t	59.40	3.23	8.20	6.85	60.37	3.45	8.80	7.28
KINAP. Isatin	Reddish brown	115 t	56.80	3.54	7.98	10.90	57.48	3.29	8.38	11.79

Where, 8 HQ=8—Hydroxyquinoline ; 1N2N=1-Nitroso-2-naphthol ; ONP=O-Nitrophenol ; PicA=Picolinic Acid ; Gly=Glycine ; Aln=β-Alanine ; & INAP=Iso-nitrosoacetophenone.

3150 cm^{-1}. The presence of the above bands in the adducts leaves little doubt that the proton is located in the ring nitrogen of the ligand and is hydrogen bonded (N...H...O). The strong bands found in the complex under investigation in 1700-1750 cm^{-1} regions are assigned to C=O vibrations. The C=O frequency of isatin is split into 1746 (s) and 1726 (sh) cm^{-1} and the lower location of the latter is again due to the formation of hydrogen bond. These two bands have been found to be metal sensitive, with a shift of 10-15 cm^{-1}, as will be clear from the Table 2. The shift towards the lower frequency in C=O suggests that the co-ordination has taken place through oxygen of the C=O group and consequently the bond order of carbon to oxygen has decreased.

TABLE—2

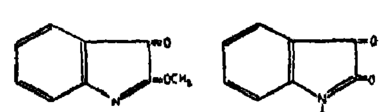
Compound	Selected IR absorption band (cm^{-1})		
	NH—Stretch	C=O	
		I (Free)	II (associated)
Isatin	3180 br	1746	1726
Li 8 HQ. Isatin	3140	1710 sh	1700
Na 8 HQ. Isatin	3120	1725 sh	1705
K 8 HQ. Isatin	3070	1725 sh	1700
K1N2N. Isatin	3180	1730	1715
KONP. Isatin	2670	1735 sh	1720
NAPicA. Isatin	2620	1730 sh	1720
KPicA. Isatin	2660	1725 sh	1715
NaGly. Isatin	2710	1730	1720
KGly. Isatin	2710	1720 sh	1695
LiAln. Isatin	2640	1720	1710
NaAln Isatin	2680	1725	1718
KAln. Isatin	2700	1722	1708
NaINAP. Isatin	2710	1720 sh	1710
KINAP. Isatin	3180 br	1740 sh	1720

It has also been observed that green coloured alkali metal salts (ML) of 1N2N usually formed brown adducts (ML.*n*.HL') with other organic acids $(HL')^1$; these ligands invariably have a replaceable proton and formed hydrogen bonding. But when the second ligand is devoid of any replaceable proton[2] (e.g., 1,10-phenanthroline), the adduct retained the green colour of the corresponding 1 : 1 salt. Isatin adducts of 1N2N formed brown adducts, suggesting again hydrogen bonding by the replaceable proton. Similar observations were noted in the case of M.ONP.Isatin adducts, when the red colour of M.ONP changed to yellowish brown in the isatin adducts after hydrogen bonding.

Isatin in absolute ethanol reacts with sodium ethoxide forming N-sodium salt. The replaceable proton attached to ring nitrogen is easily replaced by sodium metal. This easily replaceable proton of the ring nitrogen of isatin, formed hydrogen bonding with the metal salts of the organic acids.

Another feature of these adducts is that the anion L (the first ligand) must be capable of chelation to form 5- or 6-membered ring. Although *m*-nitrophenol has a high pK (=8.18), compared to ONP (=7.17), which favours adduct formation, no adduct was formed by an alkali metal salt of this with isatin, implying that preliminary chelation by the metal is essential for adduct formation.

Two methyl derivatives of isatin III and IV have been synthesised[3], and the complexing ability of these two derivatives with alkali metal salts of the



(III) (IV)

same acids were looked into. The preparative conditions remaining same, as that of the isatin adducts, we have not been able to synthesise any adduct with O-methylisatin (III), whereas under similar condi-

tions N-methylisatin (IV) formed analogous compounds as that of isatin. But N-methylisatin also did not form any isolable solid adducts with alkali metal salts of 1N2N and ONP, although characteristic colour change was observed, as shown in Table 3. The physical properties of N-methylisatin are given in Table 3.

TABLE—3

Compound	Colour	Transition or Decomposition temp. (°C)	Selected i. r. absorption band (C=O)		
N-methyl Isatin	Red	130 (m. p.)	1750 sh	1730	
Li 8 HQ. NM. Isatin	Pale yellow	240 d		1704	1692
Na 8 HQ. N.M. Isatin	Yellowish brown	225 d		1710	
NaGly. NM. Isatin	Light pink	220 d		1710	
NaAln. NM. Isatin	Deep yellow	95 d		1708	
NaPicA. NM. Isatin	Yellowish brown	190 d		1710	

The decomposition temperatures of N-methylisatin complexes except Na.Aln.NM.Isatin are higher than the isatin complex, showing their greater stability. Further, the C=O stretching bands of N-methylisatin complexes have been observed to be metal sensitive (Table 3), with appreciable shift of ca.40 cm^{-1}, suggesting that co-ordination has been through the two carbonyl oxygens. Infra-red studies also indicate that the hydrogen bonding is not an essential feature for forming these compounds.

Thus by comparing the donor properties of isatin and its two methyl ethers, it has been found that in the adducts, isatin retains the lactam structure and resemble those of the pseudo N-methyl ether.

Experimental

A. *Adducts of alkali metal salts of 8HQ, 1N2N, ONP, INAP, PicA, Gly and Aln with Isatin* :

To a saturated ethanol solution of alkali metal (Li, Na and K) salts of the acids (as mentioned above), solid isatin was added (mole ratio 1 : 3). The mixture was refluxed on a steam bath for an hour. After filtration, the coloured solution w concentrated and then allowed to cool in a refrigera tor. After 24 hours the corresponding adducts the alkali metal salts with isatin separated ou which were filtered, washed with cold absolut ethanol and dried in an oven at 80°. (Not all di yield solid adducts).

B. *Adducts of alkali metal salts of the abov mentioned acids with N- and O-methylisatin* :

The complexes of the alkali metal salts of the above mentioned organic acids with N-methylisatin, were prepared by the method entirely analogous to that described above. However, no adduct separated (and no colour change observed) when trie with O-methylisatin under similar conditions.

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Stability Constants and Thermodynamic Functions of Some Rare Earth Metal Complexes of O-Hydroxy Dibenzoyl Methane

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Potentiometric studies on thef ree ligand and the metal complexes of La(III), Pr(III), Nd(III) and Sm(III) with O-hydroxy dibenzoylmethane were carried out in 75%V/V acetone water mixture. The stability constants of these complexes formed were computed by Bjerrum—Calvin pH-titration technique, as used by Irving and Rossotti at 27.5° at an ionic strengh of 0.05M (NaCl).

A review of the literature showed that the stability constants of complexes of lanthanides with O-hydroxy dibenzoyl methane (H_2ODBM) has not been investigated. In the present work the metal-ligand stability constants and other thermodynamic functions are reported. The complexes of La^{3+}, Pr^{3+}, Nd^{3+} and Sm^{3+} formed with H_2ODBM have been studied potentiometrically by the method of Calvin and Bjerrum[1,2] improved by Irving & Rossotti[3] in 75% V/V acetone water medium. The thermodynamic stability constants were determined at 27.5° by conducting experiments at 0.025 *M* NaCl : 0.05 *M* NaCl and 0.1 *M* NaCl ionic strength. $\triangle G°$, $\triangle H°$ and $\triangle S°$ values were calculated by carrying out experiments at 27.5°, 32.5° and 37.5° respectively.

Experimental :

Materials : H_2ODBM was prepared by the procedure described in literature[4]. Rare-earth metal chlorides were prepared from their oxides. Small amount of HCl was added in stock solution to check hydrolysis. The oxides were estimated gravimetrically by oxalate method. Carbondioxide free NaOH was prepared by washing NaOH pallets first for few times by boiling double distilled water and finally dissolving it in double distilled water. 1 *M* NaCl was also prepared in double distilled water for maintaining constant ionic strength.

Apparatus :

*p*H measurements were made using a photovolt *p*H meter 112—4 with glass and calomel electrodes. The thermostatic bath maintained a temperature in the range $t \pm 0.2°$.

Bjerrum-Calvin Titrations :

For each set of experiments three titrations were carried out. The final volume in every case was 100 ml.

(i) Acid titration : Hydrochloric acid + water + acetone.

(ii) Reagent titration : Hydrochloric acid + H_2ODBM + acetone + water.

(iii) Metal titration : Hydrochloric acid + H_2ODBM + metal chloride + acetone + water.

The concentrations of HCl, H_2ODBM and metal chloride in the final volume was 0.01 *M*, 0.002 *M* and 0.0005 *M* respectively. The sodium hydroxide used was ~0.1 *M*.

An appropriate amount of sodium chloride was added to maintain constant ionic strength.

Results and Discussions :

The values of $\bar{n}_A$ at different *p*H valuse were obtained by expression[3].

$$\bar{n}_A = Y - \frac{(V'' - V')(N + E°)}{(V° + V')T_{CL}} \qquad (1)$$

where Y is the number of replaceable hydrogen ions, V' and V'' are the volumes of sodium hydroxide solution for set I and II, N, E°, T_{CL} are the initial concentration of sodium hydroxide, hydrochloric acid and total ligand concentration.

The stepwise stability constants were obtained by plotting $\bar{n}$ against pL' where $\bar{n}$ is the average number of ligands attached per metal ion and is given by

$$\bar{n} = \frac{(V''' - V'')(N + E°)}{(V° + V')\bar{n}_A T_{CM}} \qquad (2)$$

where V''' is the volume of alkali for third set and T_{CM} is total metal ion concentration. pL^- the free ligand concentration is given by

$$pL^- = \log \frac{\left\{ \sum_{n=0}^{j} \beta_n^H \left(\frac{1}{\text{antilog } pH} \right)^n (V° + V'') \right\}}{\{(T_{CL} - \bar{n}T_{CM})V°\}} \qquad (3)$$

where β_n^H is overall proton ligand stability constant. The *p*H meter was calibrated for the stoichiometric value of hydrogen ion concentration in acetone water mixture and the *p*H meter readings were thereafter taken directly for calculation.

Thermodynamic Parameters :

The value of ΔG° was obtained by expression

$$\Delta G^{\circ} = -2.303\ RT \log \beta \qquad (4)$$

ΔH° was determined with the help of an isobar equation

$$\frac{d \ln \beta}{dT} = \frac{\Delta H^{\circ}}{RT^2} \qquad (5)$$

which can also be written as

$$\frac{d \ln \beta}{d\,(1/T)} = -\frac{\Delta H}{4.576} \qquad (6)$$

The values of log β obtained at different temperatures were plotted as function of 1/T. The gradient was equated to $-H^{\circ}/4.576$. The value of ΔH° thus obtained was used to determine ΔS° according to following equation

$$\Delta H - \Delta G^{\circ} = T\Delta S^{\circ} \qquad (7)$$

The values of thermodynamic functions and stability constants are summarised in the following tables.

TABLE—1

Metal Ions	Constants	IONIC STRENGTH 0.0	0.0125	0.05	0.1
La^{3+}	log k_1	9.48	9.44	8.84	8.40
	log k_2	8.58	8.44	8.12	7.62
	log k_3	7.96	7.78	7.74	7.46
	log $\beta_{cal.}$	26.02	25.66	24.40	23.28
	log β_{exptl}	26.04			
Pr^{3+}	log k_1	9.56	9.54	9.54	8.70
	log k_2	8.66	8.50	8.32	7.92
	log k_3	8.32	8.10	8.02	7.52
	log $\beta_{cal.}$	26 64	26.24	25.46	24.14
	log $\beta_{exptl.}$	26.62			
Nd^{3+}	log k_1	9.58	9.62	9.62	9.16
	log k_2	8.88	8.78	8.48	8.10
	log k_3	8.44	8.30	8.14	7.70
	log $\beta_{cal.}$	26.90	26.70	25.78	24.62
	log $\beta_{exptl.}$	26.98			
Sm^{3+}	log k_1	9.70	9.66	9 42	9.20
	log k_2	8.90	8.88	8.62	8.34
	log k_3	8.66	8 58	8 30	7.98
	log $\beta_{cal.}$	27.28	27.12	26.34	25.52
	log $\beta_{exptl.}$	27.28			

A graph between *p*H and volume of alkali required for corresponding *p*H was plotted. A displacement in the metal titration curve with respect to ligand titration curve indicated that as complexation of metal with ligand took place, the hydrogen ions were liberated. The hydrolysis of metal ion also takes place with the liberation of protons and this process will also give a shift in metal titration curve. Since the hydrolysis of metal ion is only possible at *p*H>8 and due to the formation of precipitate at *p*H$\sim$7.5, the calculations were restricted only up to *p*H$\sim$7.0.

The $\bar{n}$ values when plotted against pL^- show two inflexions up to $\bar{n}$ values$\sim$3 (Fig. 1). Both indicate the formation of 1 : 1 ; 1 : 2 and 1 : 3 complexes. The values of pL^- at $n = 0.5$; 1.5 and 2.5 give the stability constant of 1 : 1, 1 : 2 and 1 : 3 complexes. The calculations were also carried out by least square method and spreading factor method but they do not show much difference.

The pK value for H_2ODBM was found to be 11.18 at 27.5° and 0.05 *M* NaCl ionic strength. This suggests H_2ODBM to be a strong chelating ligand and this is confirmed by high values of stability constant as indicated in the table. The value of thermodynamic stability constant was calculated by extrapolating the plot of log β vs ionic strength (μ) to the value $\mu = 0$.

Acknowledgement :

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TABLE—2

Metal Ions	Constants	Temperature 27.50	32.50	37.50	$-\Delta G^{\circ}$ KJ/MOLE	ΔH° KJ/MOLE	ΔS° J/Mole Degree
La^{3+}	K1	8.84	8.66	8.44			
	K2	8.12	8.02	7.90			
	K3	7.74	7.64	7.56			
		24.70	24.32	23.90	144.3	−343.3	−651.0
Pr^{3+}	K1	9.12	8.93	8.88			
	K2	8.32	8.29	8.08			
	K3	8.02	7.92	7.80			
		25.46	25.14	24.76	138.0	−329.9	−631.8
Nd^{3+}	K1	9.16	9.00	8.96			
	K2	8.48	8.36	8.22			
	K3	8.14	8.04	7.88			
		25.78	25.40	25.06	137.1	−217.5	−626.0
Sm^{3+}	K1	9 42	9.22	9.18			
	K2	8.62	8.56	8.38			
	K3	8.30	8·06	7.96			
		26.34	25.84	25.52	136.8	−326.8	−622.0

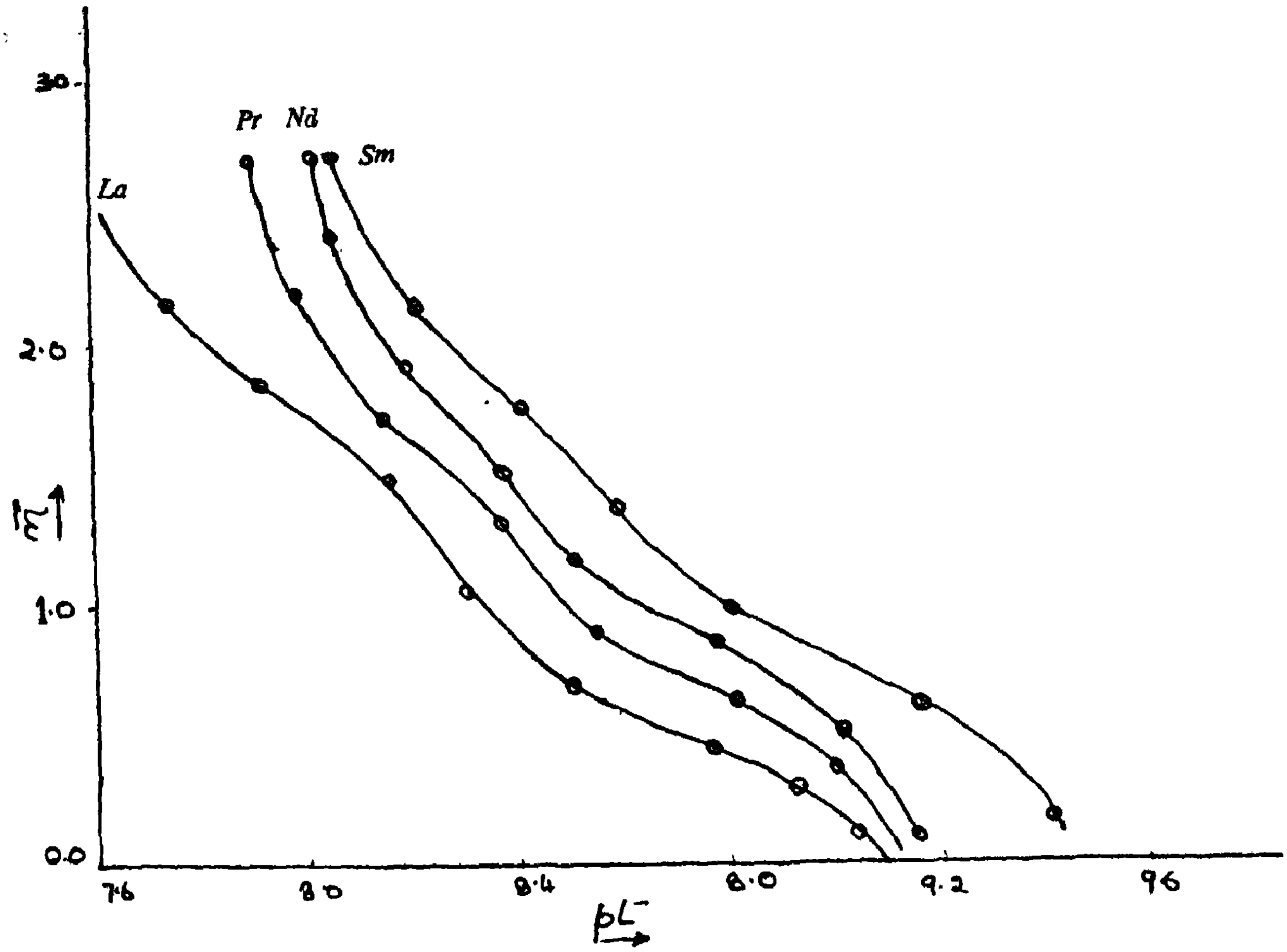


Fig. 1. Ligand O-Hydroxy Debenzoylmethane
Temp.--32.5°
Ionic Strength 0.05*M* NaCl

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Complexes of Copper with Isonitrosoacetylacetone

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$Cu(INAA)_2$ and $Cu(INAA)(CH_3COO)(H_2O)$ have been prepared and their structures have been investigated by magnetic and spectral measurements.

IT is reported that a green coloured compound[1], probably of the composition $Cu(INAA)(CH_3COO).H_2O$, is formed by the reaction of copper acetate and isonitroacetylacetone (HINAA) in aqueous solution. However, its structure has not been investigated. In the present study $Cu(INAA)_2$ and $Cu(INAA)(CH_3COO)H_2O$ have been prepared and their structures have been investigated by magnetic and spectral measurements.

Experimental

Chemicals and solvents used are of A. R. quality. The preparation of HINAA[2] and the description of the instruments employed for magnetic and spectral studies[3] are reported elsewhere.

Preparation of olive-green $Cu(INAA)_2$ (I)

An alcoholic solution of isonitroso-acetylacetone (HINAA) and an ammoniacal solution of copper (II) chloride were mixed in the molar ratio of 2 : 1 and the *p*H of the mixture was raised to 4.3 by adding dilute ammonium hydroxide solution. An olive-green compound separated rapidly on stirring. It was filtered, washed repeatedly with water, dried at 110° and analysed. (Found : Cu : 19.75% C = 37.73%, H : 3.6%, N = 8.5%; expected for $Cu(C_5H_6NO_3)_2$, Cu : 19.84%, C: 37.56%, H : 3.7% and N = 8.7%).

Preparation of Pale-green $Cu(INAA)(CH_3COO)H_2O$. (II)

An aqueous ammoniacal solution of copper acetate was mixed with an alcoholic solution of HINAA that Copper : HINAA ratio was 1 : 1. The *p*H of the mixture was raised to 4.5 by adding dilute ammonia solution. A pale-green compound separated rapidly. It was filtered, washed with water and acetone, dried at 105° and analysed. (Found Cu – 23.58%, C – 31.70%, H – 4.40%, N – 5.00%, expected for $Cu(C_7H_{11}NO_6)$, Cu – 23.61%, C – 31.29%, H – 4.10% and N – 5.20%.)

Discussion

The compounds I and II are insoluble in water and very sparingly soluble in most organic solvents. Their magnetic moments are substantially below the spin only value for one unpaired electron. The magnetic moment of I changes from 1.08 B. M. to 1.26 B. M. over the temperature range 87°-295°K, while that of II varies from 0.91 B. M. to 1.03 B.M. in the range 83.50-240°K. Such sub-normal values of magnetic moments have been reported for many copper(II) complexes[4,5]. The anomalous magnetic behaviour of I and II can be explained on the basis of antiferromagnetic interaction. The best fit for I is observed by assuming it to be a mixture of 29% of the monomeric form obeying the Curie-Weiss law with a magnetic moment of 1.9 B.M., corresponding to one unpaired electron, and 71% of the binuclear variety showing antiferromagnetic exchange interaction with exchange coupling constant, $J = 300\ cm^{-1}$ and $g = 2$. The λ_M values for the dimeric form at various temperatures are calculated by using the equation derived by Bleaney and Bowers[6].

$$\lambda_M = \frac{N\beta^2 g^2}{3\,kT} : \frac{3}{3+\exp(-J/kT)} + N\alpha$$

where terms have their usual significance. The value of $N\alpha$ is assumed to be 60×10^{-6} c.g.s/mole. Curve A in Fig. 1 shows the agreement between the observed and calculated values. The magnetic moments of II at various temperatures in the range 83.5°-240°K can be accounted for by assuming it to be a mixture of 25% of the monomeric form with a magnetic moment of 1.90 B.M. and 75% of the dimeric form exhibiting antiferromagnetic interaction with exchange coupling constant J being $300\ cm^{-1}$ and $g = 2$. The observed and calculated values for λ_M at various temperatures are represented in Curve B of Fig. 1.

The electronic spectra (Fig. 2) of I and II in methanol solution show peaks at 34.40 kK(E = 4768) and 39.46 kK (E = 2738) respectively, which are likely to be due to $\pi \rightarrow \pi^*$ transitions in the ligand. The shoulders at 28.5 kK, 25.00 kK and 17.5 kK in the spectrum of I may be assigned to charge transfer bands. However, it is possible that the shoulder near 17.5 kK arises due to a d-d transition. The diffuse reflectance spectrum (Fig. 3) (A) of I reveals a broad maximum at 14.5 kK, which is attributed to d-d transitions. The complex II in methonol solution does not show any absorption maximum in the visible region. However, its reflectance spectrum (Fig. 3B)

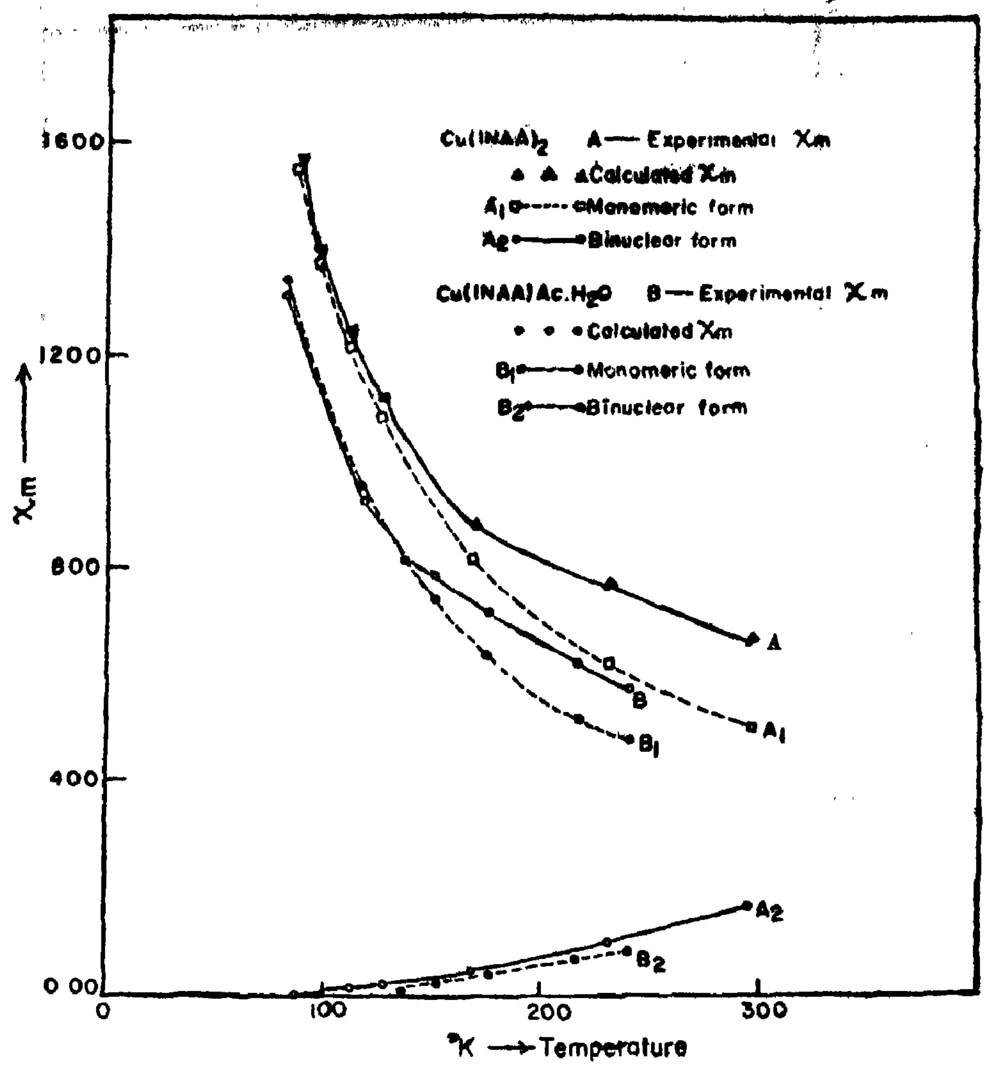
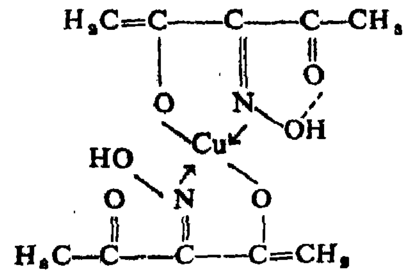


Fig. 1. Plot of X_m against temperature for $Cu(INAA)_2$ and $Cu(INAA)Ac.H_2O$ showing how experimental results could arise from a mixture of a binuclear and monomeric forms.

exhibits a broad band in the region 23-20 kK, which may be due to charge transfer transitions and/or d-d transitions.

The infra-red spectrum of I exhibits a broad maximum at 3400 cm^{-1} which, from its position and shape, is assigned to the hydrogen-bonded OH and/or bonded OH. It also reveals a broad band at 1690-1650 cm^{-1}, which may include stretching frequency of free C=O and stretching mode of C=C. The perturbed C=O and/or perturbed C=N stretching vibrations appear as a broad band near 1600 cm^{-1}. The peak near 610 cm^{-1} may be assigned to the Cu-N vibration. However, it may have a contribution from Cu-O stretching mode. The spectral and magnetic properties of I provide support to the following structures.



A

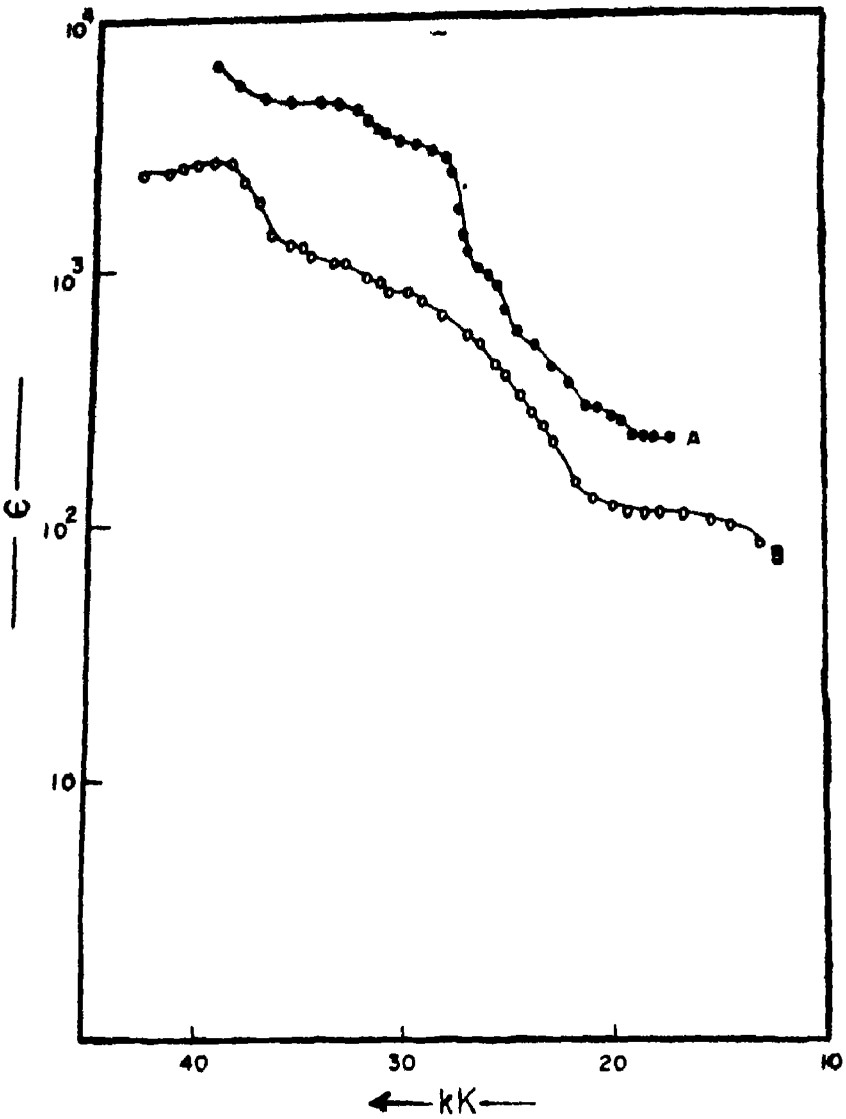
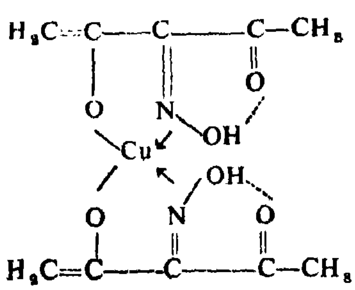
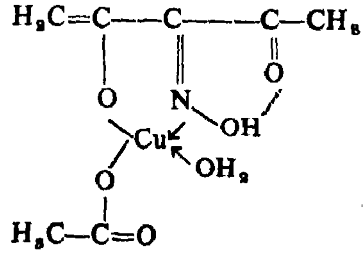


Fig. 2. Electronic Absorption Spectra of
A-Cu $(C_5H_6NO_3)_2$,
B-Cu $(C_7H_{11}NO_4)$ Complexes in Methanol



B

The infra-red spectrum of II is very similar to that of I. The present investigation suggests that the complex II may be formulated as



C

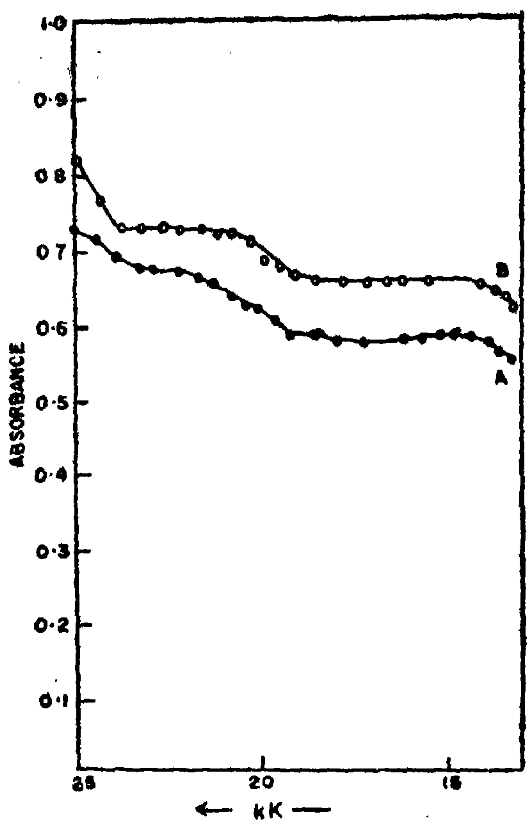
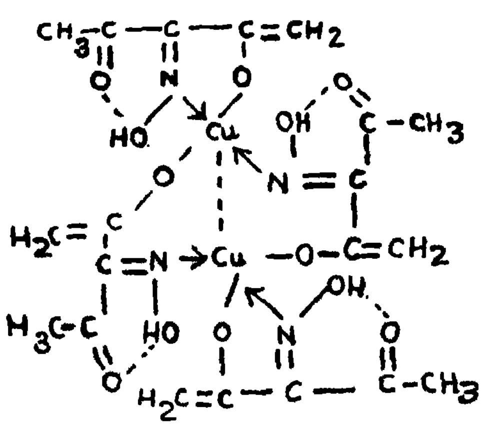
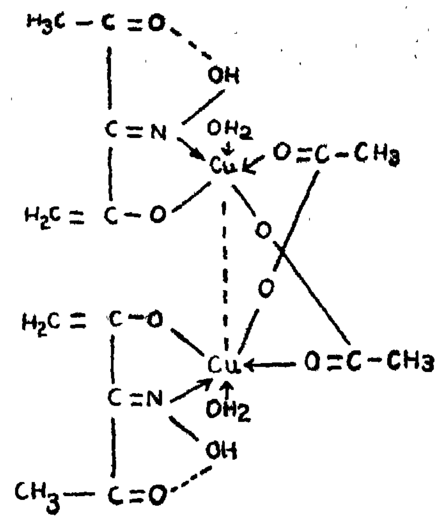


Fig. 3. Diffuse Reflectance Spectra of
A-Cu $(C_5H_6NO_3)_2$
B-Cu $(C_7H_{11}NO)$

The likely structures for the dimeric forms of I and II, which exhibit anti-ferromagnetic intraction, are shown below



D



E

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Structural Investigations of Co(III) and Rh(III) Complexes of α-Benzilmonoxime*

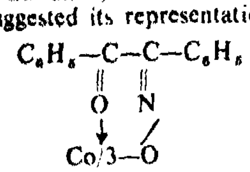
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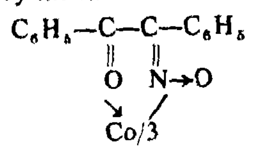
Manuscript received on 22 March 1977, accepted 23 August 1977

Magnetic and spectral data suggest that $Co(BMO)_3$ and $Rh(BMO)_3$ are octahedral and have five-membered chelated ring structures involving bonding through oxygen and nitrogen donor atoms.

TRIS-(α-benzilmonomimato) cobalt(III), $Co(BMO)_3$ has been assigned the structure I by Taylor and Ewbank[1], while Pfeiffer and Richarz[2] have suggested its representation by the structure II.



I



II

However, its structure has not been studied by physico-chemical methods. In the present study the structures of $Co(BMO)_3$ and $Rh(BMO)_3$ have been investigated by magnetic measurements and NMR, I.R., visible and u.v. spectroscopy. The synthesis of $Rh(BMO)_3$ has not been reported earlier in the literature.

Experimental

Chemicals and reagents used were of A.R. grade. α-Benzilmonoxime (HBMO) and $Co(BMO)_3$ were prepared by the methods recommended by Welcher[3]. $Co(BMO)_3$ was further purified by recrystallization from chloroform and analysed. (Required for $Co(BMO)_3$: Co-8.06%, C-68.96%, H-4.10%, N-5.74%, Found : Co-8.09%, C-67.98%, H-4.30%, N-5.70%). Rh $(BMO)_3$ was prepared by adding a solution of 0.26 g of HBMO in 30 ml of ethanol to 10 ml of 1% solution of $RhCl_3$ in aqueous-hydrochloric acid. A brick-red coloured complex was obtained. It was separated, recrystallised twice from benzene, dried at 110° and analysed for Rh, C, H and N (Required for Rh $(BMO)_3$: Rh-13.28%, C-64.88%, H-3.87%, N-5.42%, Found : Rh-13.32%, C-64.00%, H-3.90% N-5.40%).

Instruments employed are described elsewhere[4,5]. Ethylenedibromide was used as a solvent in the determination of molecular weight of Co $(BMO)_3$ by the freezing point depression method.

Results and Discussion

$Co(BMO)_3$ (red) and $Rh(BMO)_3$ (brick-red) are soluble in organic solvents, insoluble in water and nonionic in nitrobenzene solution. The former is monomeric in ethylenedibromide solution. Both the complexes are diamagnetic, indicating octahedral structure involving d^2sp^3 hybridisation.

The PMR spectrum (Fig.1) of HMBO in dioxane exhibits a peak at-1.1τ (with respect to TMS), which is assigned to the =NOH group. Two bands near 1.70 τ and 2.20 τ are attributed to proton resonance signals from $-C_6H_5$ group. Co $(BMO)_3$ in $CDCl_3$ reveals these bands at 2.67 τ and 2.70 τ, while Rh $(BMO)_3$ in $CDCl_3$ exhibits them at 2.69 τ and 2.73 τ. The metal complexes do not show a signal due to the =NOH group suggesting the replacement of the oxime proton by the metal.

Co^{59} resonance signal (Fig.2) in $CDCl_3$ solution of Co $(BMO)_3$ is observed at a slightly higher field from that of tris-(ethylenediamine) cobalt(III) and is away from that of tris-(acetylacetonato) cobalt(III). Considering the relation between the chemical shift and the ligand field strength shown by Griffith and Orgel[6], it is inferred that the ligand field strength of anion BMO^- is higher than that of ethylenediamine. The structure I for $Co(BMO)_3$ would imply that the ligand field due to the anion BMO^- should be close to that of acetylacetonate ion and much less than that of ethylenediamine. The chemical shift of Co^{59} in $Co(BMO)_3$ seems to support the structure II proposed by Pfeiffer and Richarz.

The infra-red spectra of the reagent α-benzilmonoxime (HBMO), partially deuterated HBMO, $Co(BOM)_3$ and $Rh(BMO)_3$ in CsBr disc have been examined in the region 4000-250 cm^{-1}. The broad band around 3440 cm^{-1} in HBMO is assigned to hydrogen bonded –OH stretching frequency (Fig. 3.). This assignment is further confirmed by the appearance of a new band at 2508 cm^{-1} in the spectrum of the partially deuterated HBMO. One of the important features of the infra-red spectra of $Co(BMO)_3$ and $Rh(BMO)_3$ is the absence of OH-stretching frequency in the region 3600 – 3200 cm^{-1} (Fig. 4). This suggests that the hydrogen of the oxime group –NOH is replaced by the metal atom

* Part of this work was presented at the XVth International Conference on Coordination Chemistry held in Moscow, U.S.S.R., 27-30 June, 1973.

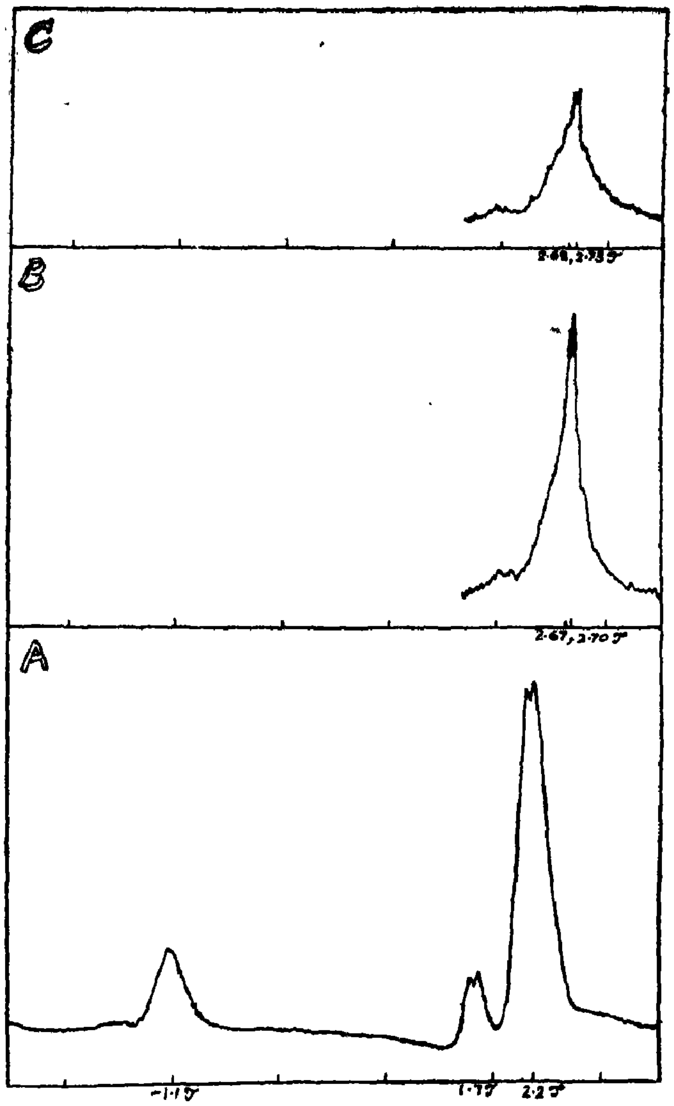


Fig. 1 PMR spectra of (A) HBMO, (B) $Co(BMO)_3$ and (C) Rh $(BMO)_3$

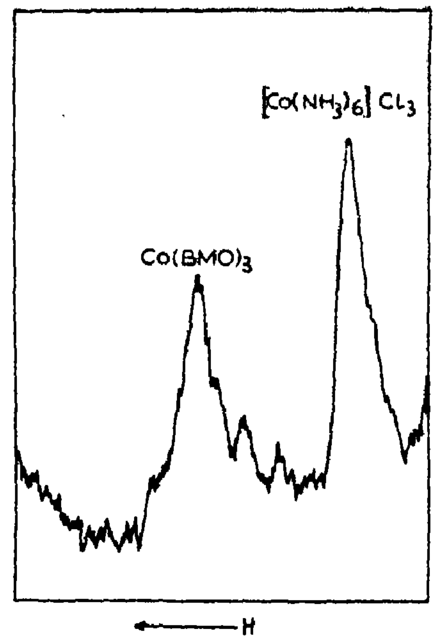
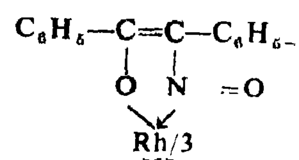


Fig. 2 NMR spectrum of Co in a $CDCl_3$ solution of $Co(BMO)_3$

on complexation, which is in good agreement with the results of PMR studies. The two complexes, HBMO and deuterated HBMO exhibit C=H stretching frequency near 3080 cm^{-1}. The bands due to the monosubstituted phenyl in HBMO appear at 1595 cm^{-1}, 1572 cm^{-1}, 1495 cm^{-1}, 1440 cm^{-1}, 762 cm^{-1} and 688 cm^{-1}. These bands are observed more or less at the same position in the spectra of deuterated HBMO, Co $(BMO)_3$ and $Rh(BMO)_3$.

The strong absorption at 1675 cm^{-1} in HBMO is not shifted on deuteration and therefore it is assigned to C=O of an aromatic ketone. The peak near 1650 cm^{-1} is attributed to C=N stretching frequency. The two bands at 1608 cm^{-1} and 1515 cm^{-1} in the spectrum of $Co(BMO)_3$ may be attributed to perturbed C=O and/or C=N stretching frequencies. This implies that the complexation leads to the bonding through oxygen and nitrogen atoms of HBMO as expected on the basis of the five membered ring structure II. The spectrum of $Rh(BMO)_3$ is similar to that of $Co(BMO)_3$, except that it shows two additional bands at 1640 cm^{-1} and 1670 cm^{-1}. The reasons for their presence are not obvious. One possibility is that one of the bands is associated with –C=C– stretching frequency which may arise due to the structure III. Apparently


III

these bands are very weak in Co $(BMO)_3$.

The structures *II* and *III* suggest the presence of

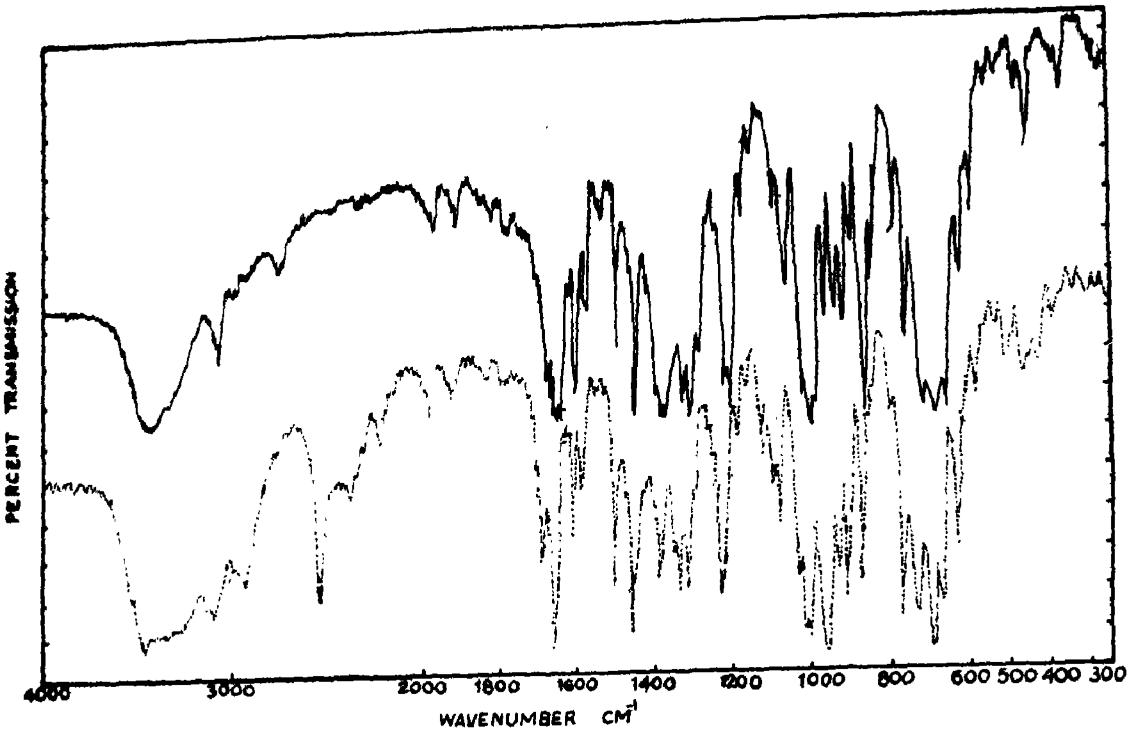


Fig. 3. Infrared Absorption Spectra of α-Benzilmonoxime (——) and Deuterated α-Benzilmonoxime (......)

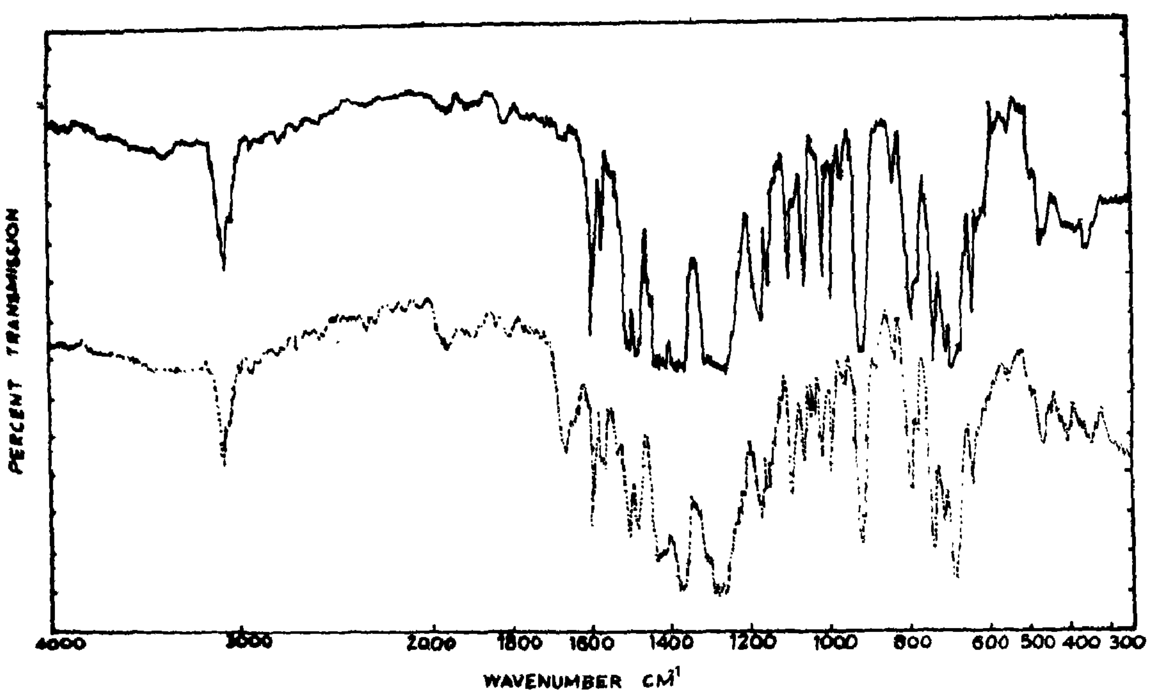


Fig. 4. Infrared Absorption Spectra of $Co(BMO)_3$ (——) Complex and $Rh(BMO)_3$ (......) Complex

N→O, N=O and metal-nitrogen stretching frequencies. The bands at 1215 cm^{-1} and 1945 cm^{-1} in HBMO are not shifted on deuteration and so they are assigned to N—O stretching. These bands are shifted respectively to 1268 cm^{-1} and 1182 – 1184 cm^{-1} in $Co(BMO)_3$ and $Rh(BMO)_3$, which suggests increase in the double bond character of N—O linkage on complex formation. This is consistent with the five-membered ring structures II & III. The six-membered ring structure I proposed by Taylor and Ewbank would require the reduction of the double bond character of the N—O linkage due to the formation of M—O and the shift of N—O frequency towards the lower wavenumber side.

Both $Co(BMO)_3$ and $Rh(BMO)_3$ exhibit a

number of bands in the range of 700-300 cm^{-1}. It is difficult to assign them without any ambiguity, because HBMO also shows bands in this region.

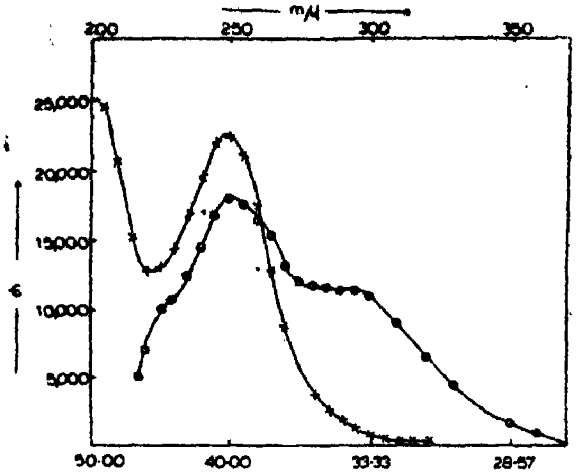


FIG 5 ELECTRONIC SPECTRA OF α-BENZILMONOXIME IN
1) 0·01 N NaOH SOLUTION (-o-o-o-)
2) METHANOL SOLUTION (-x-x-x-)

The ultra-violet spectrum of HBMO in methanol solution exhibits a high intensity absorption maximum at 40.00 kK ($\epsilon = 22{,}800$), which is attributed to $\pi \rightarrow \pi^*$ transition. In 0.1 *N* NaOH it reveals a shoulder near 34.48 kK in addition to the strong band at 40.00 kK ($\epsilon = 18{,}200$) (Fig. 5). Both $Co(BMO)_3$ and $Rh(BMO)_3$ in methanol exhibit a $\pi - \pi^*$ transition band in the ligand near 40.00 kK, the molar extinction coefficients being 31,700 and 37,600 respectively (Fig. 6). $Co(BMO)_3$ shows an intense absorption maximum at 34.48 kK ($\epsilon = 30{,}800$) which may also be due to a $\pi \rightarrow \pi^*$ transition in the ligand. This band is not observed in the spectrum of $Rh(BMO)_3$.

The charge transfer transitions in $Co(BMO)_3$ and $Rh(BMO)_3$ seem to appear as a broad maximum in the region 23.81-29.85 kK. The d-d transitions in these complexes are not observed because they are probably obscured by the tail-end of the high intensity charge transfer bands. The reflectance spectra of the complexes reveal a peak in the region 33.33-38.46 kK in addition to a diffuse maximum in the range 20.00-28.57 kK (Fig. 7).

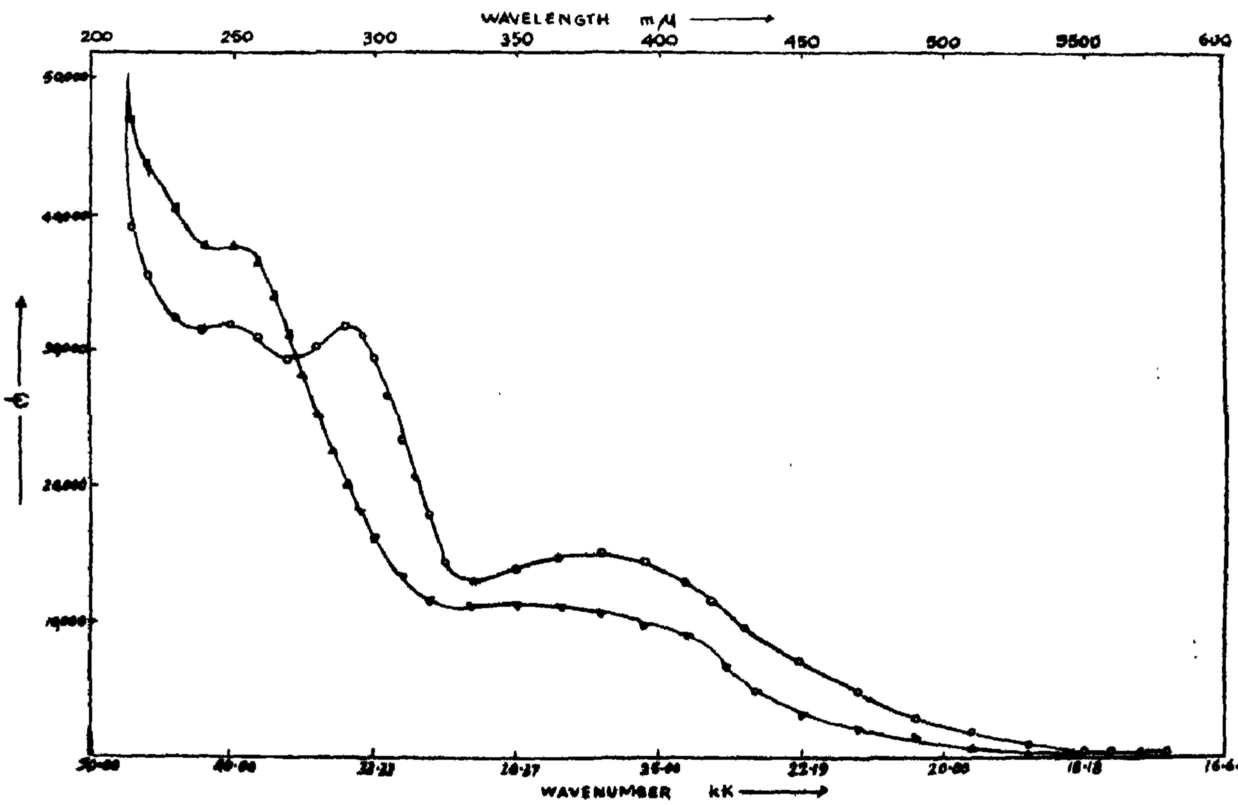


Fig. 6. Electronic Spectra of $Co(BMO)_3$ (-o-o-o-) and $Rh(BMO)_3$ (Δ-Δ-Δ) in methanol.

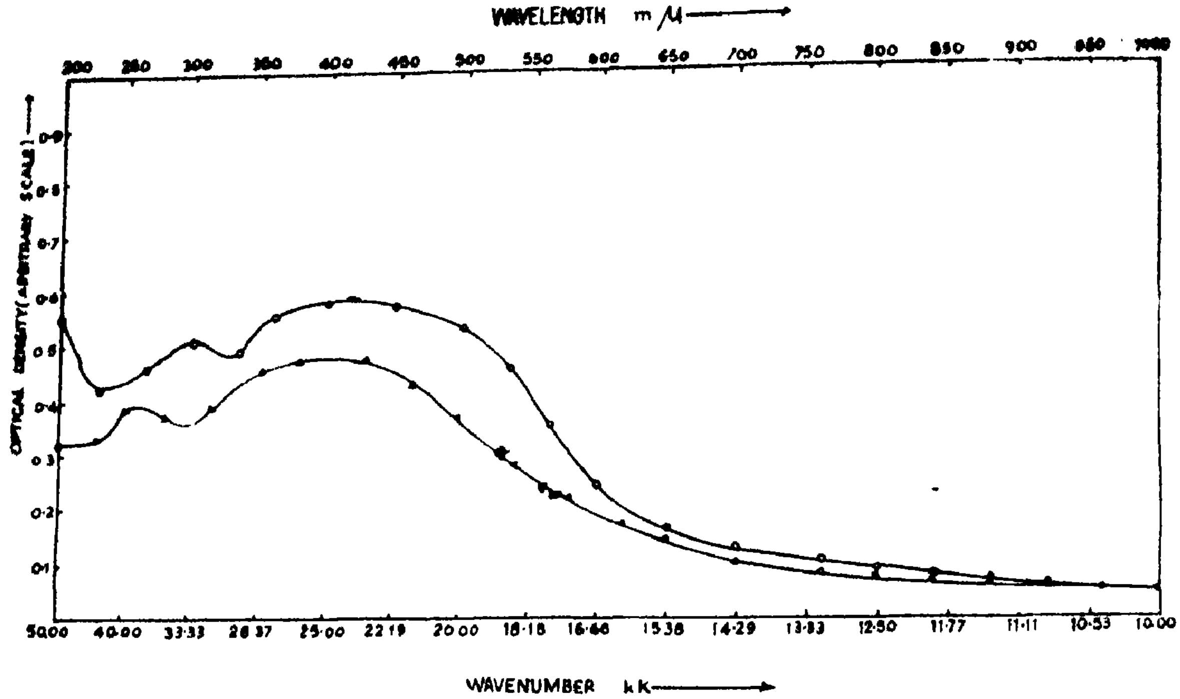


Fig 7. Reflectance Spectra of $Co(BMO)_3$ Complex (-o o-o-) and $Rh(BMO)_3$ Complex (Δ-Δ-Δ)

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Chromium(III) Heterocomplexes—Part. III
Isothiocyanato-complexes of Chromium(III) with Some Bidentate Benzimidazoles

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Isothiocyanato-complexes of chromium(III) with some bidentate benzimidazole derivatives, such as 2-(2'-pyridyl)-, 2-(2'-hydroxyphenyl)-, and 2-(2'-aminophenyl)-benzimidazole, have been prepared by replacement in $K_3[Cr(NCS)_6]$. Infrared spectral studies suggest N-nonded thiocyanate. Room-temperature magnetic moments lie between 3.65 and 3.83 B.M. The $10D_q$ values (18,000-19,000 cm^{-1}), calculated from ${}^4A_{2g} \rightarrow {}^4T_{2g}$ transitions, lie above that for $Cr(NCS)_6^{-3}$ (17,800 cm^{-1}).

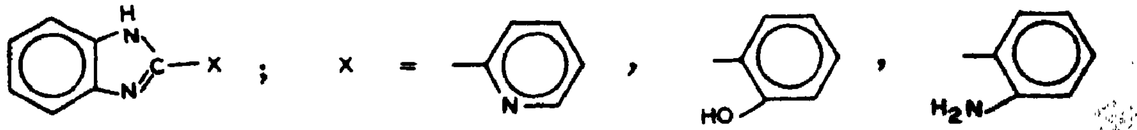
IN a previous communication[1], the isothiocyanato-complexes of chromium(III) with monodentate benzimidazole (I, X=H) and 2-methylbenzimidazole (I, $X=CH_3$) were reported. On account of the biological importance the benzimidazole chemistry has gained[2], it is considered worthwhile to examine the complex-forming behaviour of some bidentate ligands of this class, such as 2-(2'-pyridyl)benzimidazole (II, PyBzH), 2-(2'-hydroxyphenyl)benzimidazole (III, HO-PhBzH). and 2-(2'-aminophenyl) benzimidazole (IV, H_2N-PhBzH).

2-(2'-Pyridyl) benzimidazole is almost comparable to 2, 2'-bipyridyl and 1,10-phenanthroline on account of common donor system -N=C-C=N- and the coordinating behaviour of this ligand has been studied for many metals enumerated in one of our communications[3]. The chelating behaviour of 2-(2'-hydroxyphenyl)benzimidazole has attracted the attention of chemists since the infra-red studies were made by Harkins et al[4]. The replacement of the -OH group by an $-NH_2$ group (IV) will lead to the change in coordination site from N, O to N, N.

derivatives were prepared by usual method of condensation of *o*-phenylenediamine with picolinic acid for PyBzH[5], with salicylamide for HO-PhBzH[6], and with anthranilic acid for H_2N-PhBzH[7]. Purities of these compounds were checked by their melting points and nitrogen analyses.

Potassium hexathiocyanatochromate(III) was prepared by the method described in literature[8].

Preparation of Complexes : Potassium hexathiocyanatochromate(III) and the ligand in 1 : 2 molar proportion were refluxed in 95% ethanol on steam-bath till a permanent change in colour was observed (15-30 minutes). The ligand could not be used in bigger proportion for the fear of its precipitation in the subsequent step of dilution with water. The liquid was cooled, filtered and diluted with a large volume of water when a solid separated in every case. The solid was collected on filter, washed thoroughly with water, and purified by reprecipitation from ethanolic solution. The purified samples were dried in air.



I II III IV

Chromium(III) salts do not appear to react with these ligands directly to form any complex with definite composition. A reaction of PyBzH with chromium(II) halide, followed by aerial oxidation, lead to the formation of halo-bridged complex[3] of the composition $[Cr(PyBz)_2X]_2$. Direct replacement in $Cr(NCS)_6^{-3}$ has been attempted at in the present investigation.

Experimental

Preparation of the ligands : The benzimidazole

In the case of 2-(2'-aminophenyl)benzimidazole, the filtrate, collected from the separation of brown solid (no. 3, table 1) on dilution with water, was coloured red and on concentration and cooling, gave reddish pink crystals of a mono-chelated complex (no. 4, table 1), which were filtered and dried in air.

Physical Measurements : Electrical conductances were measured with Philips PR 9500 resistance bridge using dip-type cell. Magnetic moments were determined on a Gouy magnetic balance,

*For correspondence

TABLE 1. ANALYTICAL DATA, ELECTRICAL CONDUCTANCES ($OHM^{-1} CM^{2} MOLE^{-1}$ IN 95% ETHANOL AT 308°K) AND MAGNETIC MOMENTS (308°K).

S. No.	Complex	Colour	Elemental Analyses % Cr Found.	% Cr Reqd.	% C Found	% C Reqd.	% H Found	% H Reqd.	% N Found.	% N Reqd.	Conductance.	μ_B
1.	$[Cr(PyBzH)(NCS)_2OH.H_2O]$. 1.5$C_2H_5OH$	Brown	11.20	11.12	43.23	43.67	4.14	4.53	15.40	14.98	12.0	3.88
2.	$[Cr(HO-PhBzH)(O-PhBzH)(NCS)_2]$. 3$C_2H_5OH$	Bluish green	7.19	7.16	56.74	56.26	4.72	5.14	12.19	11.58	37.0	3.65
3.	$[Cr(H_2N-PhBzH)(H_2N-PhBz)(NCS)_2]$, 2.5$C_2H_5OH$ 3H_2O	Brown	6.93	6.89	52.98	52.49	5.75	5.61	14.91	14.84	16.0	3.66
4.	$[Cr(H_2N-PhBzH)(NCS)_2OH.H_2O]$, 2$C_2H_5OH$. 3$H_2O$	Reddish pink	10.00	9.78	43.41	42.92	5.23	5.50	13.00	13.17	25.0	*

* could not be determined on account of very low yield of the complex.

calibrated with $Hg[Co(NCS)_4]$[9]; diamagnetic corrections were made using Pascal's constants[10]. Electronic absorption spectra were recorded on Beckman DK-2A Ratio Recording Spectrophotometer using matched silica cells. The infra-red spectra were scanned on Beckman IR-20 and IR-12 Spectrophotometers in KBr discs.

Results and Discussion

Thiocyanate groups are only partially replaced by the bidentate benzimidazoles under investigation and the stoichiometry of the compounds are shown in *table 1*, which are supported by their electrical conductance values. 2-(2'-Pyridyl)benzimidazole coordinates through the two tertiary nitrogen atoms, the imidazole-NH remaining intact; this is in contrast to the observations made in the binuclear halo-bridged chromium(III) complexes with this ligand reported earlier[3]. The phenolic OH of one 2-(2'-hydroxyphenyl)benzimidazole molecule in the bis-chelate is presumably deprotonated. 2-(2'-Aminophenyl)benzimidazole gives rise to two chelates: (i) a bis-chelated brown complex containing one deprotonated and the other undeprotonated ligand molecule, and (ii) a mono-chelated reddish pink complex containing an undeprotonated ligand.

As expected for a $3d^3$ ion with a ground state term, the room-temperature magnetic moment values (table 1) indicate the existence of chromium(III) in octahedral environment without any appreciable orbital- or TIP-contribution.

Infra-red Spectra

The infra-red spectrum of each complex has been compared with that of the ligand and important observations have been noted in table 2.

The NH stretching frequencies of the ligands, which lie between 3010 and 3040 cm^{-1}, are shifted to higher frequency side in the complexes by 5-20 cm^{-1}. Harkins et al[4]. reported that there was a decrease in the NH stretching frequency of the pyridyl or the hydroxyphenyl derivatives on complexation with metals like copper(II), nickel(II), and zinc(II), but quite a good number of evidences has accumulated[11] to show that there is no regularity in this trend.

Strong CN stretching bands near 2065-2075 cm^{-1} indicate N-bonded terminal thiocyanate. CS stretching frequency, which is more useful in distinguishing M-NCS and M-SCN isomers[12], were diagnostic[1] of M-NCS bonding in complexes with benzimidazole and 2-methylbenzimidazole. These bands, however, could not be identified in the complexes under present investigation as the out-of-plane bending mode of the 1 : 2-disubstituted aromatic rings or the pyridine nucleus at the 2-position of the imidazole ring also appeared in the same region[18]. The NCS bending has been more profitably used[12] in elucidating the linkage of thiocyanate group; N-bonded thiocyanate has this band near 450-490 cm^{-1}, whereas S-bonding lowers this to 400-440 cm^{-1}. The fact that all complexes under investigation show bands of medium intensity at 490 cm^{-1} confirms the existence of N-bonded thiocyanate groups, which is in accordance with the general view that elements of the first transition series form M-NCS bonds rather than M-SCN ones[19].

TABLE 2—INFRA-RED FREQUENCIES (CM^{-1}) IN KBR DISCS AND ELECTRONIC ABSORPTION BANDS (CM^{-1}) IN 95% ETHANOL.

S. No.	Complex	NH Stretching*	Thiocyanate Vibrations ν (CN)	δ (NCS)	$^4A_{2g} \longrightarrow {}^4T_{2g}$ ($10D_q$)
1.	$[Cr(PyBzH)(NCS)_2OH.H_2O]$, 1.5$C_2H_5OH$	3060 s (3040)	2065 vs	490 m	18,420
2.	$[Cr(HO-PhBzH)(O-PhBzH)(NCS)_2]$, 3$C_2H_5OH$	3035 s (3030)	2070 vs	490 m	18,180
3.	$[Cr(H_2N-PhBzH)(H_2N-PhBz)(NCS)_2]$, 2.5$C_2H_5OH$ 3H_2O	3040 s (3025)	2075 vs	490 m	19,050
4.	$[Cr(H_2N-PhBzH)(NCS)_2OH.H_2O]$, 2$C_2H_5OH$.3$H_2O$	3045 s (3025)	2070 vs	490 m	18,690

*NH Stretching frequencies of organic ligands in parentheses.
Abbreviations: vs = very strong; s = strong, m = medium intensity.

Electronic Spectra

The electronic spectra (table 2) exhibit only one band on account of the transition $^4A_{2g} \rightarrow {}^4T_{2g}$ near 525-550 nm in each complex. The 10Dq values of these complexes are higher than that of $Cr(NCS)_6^{-3}$ (17,800 cm^{-1}) and so, presumably, the substitution takes place easily. A comparison of the hydroxoaquo-complexes of PyBzH and $H_2N-PhBzH$ and diisothiocyanato-complexes of HO-PhBzH and $H_2N-PhBzH$ suggest the following relative positions of these ligands in spectrochemical series : $H_2N-PhBzH \sim PyBzH > HO-PhBzH$.

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Studies on the Complexes of Some Triphenyl Methane Dyes with Chromium, Molybdenum and Tungsten

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Crystal violet, malachite green and fuchsine react with potassium chromate, sodium molybdate and sodium tungstate in 1N H_2SO_4 to give 1 : 1 metal ligand complexes. However, in the case of chromate only an addition product with these cationic dyes is obtained. Infra red spectra of the isolated complexes show that the dyes are bound to the metal through the nitrogen atom.

TRIPHENYL methane (TPM) dyes have been used in potentiometric titrations[1] and in spot test analysis[2]. Recently we had used these dyes for the spectrophometric[3] estimation of Ce(IV) and also studied the nature of the complexes[4] formed by them with Ce(IV). These studies have now been extended to the complexes of triphenyl methane dyes with chromium, molybdenum and tungsten.

Experimental

Materials used

Potassium chromate, sodium molybdate and sodium tungstate were AnalaR grade (B. D. H.) reagents. Their solutions were prepared in double distilled water and their strengths determined by the usual methods.[5]

Crystal violet, malachite green and fuchsine dyes were B.D.H. products and were purified by recrystallisation from 50% alchohol before use. Their purity was tested by thin layer chomatography and were found to give a single spot.

Equipment

Spectrophotometric studies were carried out on Bausch and Lomb spectronic 20 spectrophotometer using 10 mm glass tubes. Polarographic studies were carried out at 25 with a Cambridge pen recording polarograph using a Fischer capillary. The capillary characteristic was 3.75 $mg^{2/3}$ $S^{-1/2}$. The solutions were deaerated by bubbling pure nitrogen gas for 10 minutes in an H-type cell.

Infrared spectra were recorded on Beckmann I.R. 20 spectrophotometer in KBr pellets. Magnetic measurements were carried out by Gouy's method at room temperature.

Isolation of the Complexes :

100 ml of 0.1M sodium molybdate, sodium tungstate or potassium chromate in 1N H_2SO_4 was mixed with 100 ml of 0.1M TPM dye in 1N H_2SO_4 and the solution shaken vigorously for a few minutes. After 15 minutes, the complex got precipitated. The precipitate was filtered off, washed with some 1N H_2SO_4, water, then alchohol and finally with ether. It was dried in vacuum over anhydrous calcium chloride.

Analysis of the complexes :

The complex was fused with fusion mixture and the fused mass extracted with water. The extract was boiled for about 5 minutes and heated to dryness on a low flame. The residue was extracted with dilute NaOH in the case of molybdenum and tungsten and with dil. HCl in the case of chromium complexes. Molybdenum and tungsten were then estimated as their oxides[5] while chromium was estimated with potassium ferrocyanide[6] after reducing to chromium(III) with H_2O_2. SO_4^{--} in the extracts of Mo and W was estimated as $BaSO_4$. Nitrogen and carbon content of the complexes were obtained through the kind courtesy of the microananlytical laboratories, I.I.P., Dehradun (India).

Results and Discussion

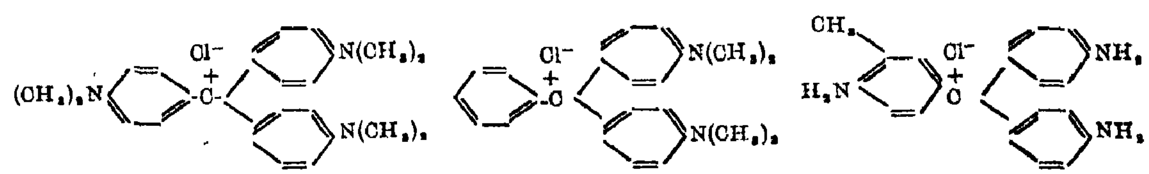
Crystal violet, malachite green and fuchsine form 1 : 1 soluble complexes with potassium chromate, sodium molybdate and sodium tungstate in 1N H_2SO_4 in the concenteration range of $10^{-3}M$. At higher concentrations (0.1M) of the metal and dyes the complexes separate out as precipitates. The solutions of the complexes show new regions of absorption in the visible region as listed in Table 1. A 1 : 1 stoichiometry for these complexes was found by continuous variation, molar ratio and polarographic methods. Spectrophotometry could not be employed for molybdenum complexes as they give very light colour in dilute solutions.

In increasing concentration of the dyes, the polarographic $E_{1/2}$ of the reversible waves show a shift towards more negative potentials, giving a linear $E_{1/2}$ versus log C plot, whose slope, Δ $(E_{1/2})c/\Delta$

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TABLE 1—CHEMICAL ANALYSIS, ABSORPTION MAXIMA, POLAROGRAPHIC DATA OF THE T.P.M. DYE COMPLEXES

Complex		% Metal	% Carbon	% Nitrogen	% Hydrogen	% Sulphate	Colour	Absorption maxima λnm	$\Delta(E_{1/2})_0 / \Delta \log C$	Stability constant (from polarography) log K.
$C_{25}H_{30}N_3HCrO_4\ 2H_2O$	Calc.	9.9	57.1	8.0	6.6	—	Brownish	455	—	—
Crystal violet	Found.	10.8	57.0	8.2	6.8	—				
$C_{23}H_{25}N_2HCrO_4\ 2H_2O$	Calc.	10.7	57.2	5.8	6.2	—	Brownish	455	—	—
Malachite green	Found.	10.3	57.9	5.8	5.8	—				
$C_{20}H_{20}N_3HCrO_4\ 2H_2O$	Calc.	11.4	52.7	9.2	5.5	—	Brownish	440	—	—
Fuchsine	Found.	11.1	52.8	9.0	5.5	—				
$MoO_2(CV)SO_4,4H_2O$	Calc.	13.6	42.6	5.9	5.3	13.6	Greenish	—	0.06	3.46
	Found.	13.7	42.3	5.4	5.1	13.3				
$MoO_2(MG)SO_4,4H_2O$	Calc.	14.5	41.8	4.2	5.0	14.5	Greenish	—	0.06	4.02
	Found.	14.1	42.0	4.2	4.9	13.9				
$MoO_2(FU)SO_4,4H_2O$	Calc.	15.1	37.8	6.6	4.4	15.1	Light	—	0.05	3.70
	Found.	14.8	37.5	6.0	4.5	15.0	Violet			
$WO_2(CV)SO_4,4H_2O$	Calc.	23.2	37.8	5.3	4.8	12.1	Green	630	0.05	2.50
	Found.	22.9	37.3	5.0	4.4	11.8				
$WO_2(MG)SO_4.4H_2O$	Calc.	24.5	36.9	3.7	4.4	12.8	Green	630	0.05	3.8
	Found.	24.2	36.8	3.6	4.2	12.6				
$WO_2(FU)SO_4.4H_2O$	Calc.	25.4	32.2	5.8	3.8	13.3	Violet	575	0.08	4.1
	Found.	25.5	33.5	5.8	3.7	12.8				



CV = Crystal violet MG = Malachite green Fu = Fuchsine

TABLE 2—INFRA RED SPECTRAL DATA (cm^{-1}) OF THE TPM DYE COMPLEXES

CV	Complex of CV with			MG	Complex of MG with			FU	Complex of FU with			Assignment
	Cr.	Mo	W		Cr	Mo	W		Cr.	Mo	W	
—	3400	3400	3400	—	3400	3400	3400	—	3400	3400	3400	$\nu(H_2O)$
—	—	—	—	—	—	—	—	3300	3300	3200	3200	$\nu(NH_2)$
2840	2840	—	—	2840	2840	—	—	—	—	—	—	$N(CH_3)_2$
2800	2800	—	—	2800	2800	—	—	—	—	—	—	
—	1580	1600	1610	—	1600	1600	1600	—	1600	1620	1620	H_2O
1350	1350	1340	1340	1350	1350	1340	1340	—	—	—	—	ν(C–N) of $C-N(CH_3)_2$
—	—	—	—	—	—	—	—	1260	1260	1180	1180	ν(C–N) of $C-NH_2$
—	—	1100	1100	—	—	1100	1120	—	—	1130	1110	$\nu(SO_4^-)$
—	—	980	960	—	—	960	970	—	—	950	950	W=O, MO=O
—	900	—	—	—	910	—	—	—	880	—	—	CrO_4^{--}
—	—	840	800	—	—	800	800	—	—	800	800	(H_2O) Co-ordinated
—	—	640	650	—	—	640	620	—	—	620	640	
—	—	580	580	—	—	570	575	—	—	570	580	νM–N

log C, gave the value of p, the complexing number, by Lingane's method[7] for reversible waves. The value of p was found to be one in all the cases (Table 1) showing the formation of 1 : 1 complexes. (Log analysis showed the value of n to be 1.).

In 1*N* H_2SO_4, MoO_2^{++} and WO_2^{++} species exist[8] and their complexes can be formulated as MoO_2 (T.P.M. dye) SO_4. $4H_2O$ and WO_2 (T.P.M. dye) SO_4. $4H_2O$ while for chromium, the anion CrO_4^{--} in the stable species an addition product [T.P.M. dye. $HCrO_4$] $2H_2O$ is formed (Analysis : Table 1).

The important infra-red spectral characteristics of the complexes and the dyes are given in table 2. All the complexes show a broad band at 3400 cm^{-1} and around 1600 cm^{-1} corresponding to water. The complexes of molybdenum and tungsten also show bands around 850 cm^{-1} and 650 cm^{-1}, which may be assigned to the rocking and M-O stretching of co-ordinated water[9] where as the chromium compounds contain no co-ordinated water. The appearance of bands at 3400 cm^{-1} and around 1600 cm^{-1} indicates that water may be only weakly co-ordinated in these complexes (strong aquo complex-

ation lowers the H_2O frequency[11] by 300 cm^{-1} and raises the bending frequency by some tens of cm^{-1}). Infrared spectra also shows a sharp band of medium intensity around 950 cm^{-1} corresponding to W=O and Mo=O in the complexes of tungsten and molybdenum[10]. The complexes of chromium show bands characteristic of CrO_4^{--} in the 900 cm^{-1} region[9]. The presence of SO_4^{--} in the complexes of molybdenum and tungsten is also confirmed by the band appearing around 1100 cm^{-1}. The coordination of the dye takes place through nitrogen and is evidenced by the appearance of the metal-nitrogen stretching band in the 580-570 cm^{-1} region for molybdenum and tungsten complexes. This band is absent in the case of chromium complexes, suggesting that an addition product through ionic interaction may be present. The shift in C–N stretching of C-N $(CH_3)_2$ grouping (appearing at 1350 cm^{-1} in M.G. and C. V.) in the complexes of malachite green and crystal violet and C-N stretching of C-NH_2 group in fuchsine complex (appearing at 1200cm^{-1} in the fuchsine dye) shows co-ordination of the dye through nitrogen[4] of this group. The $-N(CH_3)_2$ group in malachite green and crystal violet shows two bands around 2800 cm^{-1} which disappear on coordination through nitrogen with the metal[11]. The asymmetric NH_2 stretching shows shifts from around 3300 cm^{-1} to around 3200 cm^{-1} in the case of fuchsine, which confirms co-ordination of fuchsine through nitrogen of the NH_2 group. In the case of chromium compounds neither the C-N stretching (in 1300 cm^{-1} region) of the dye shows shifts nor the $-N(CH_3)_2$ bands around 2800 cm^{-1} disappear showing thereby that only an addition product is formed.

These dyes act as bidentate ligands[4]. In crystal violet all the three N $(CH_3)_2$ groups are equivalent and hence any two such groups can enter into co-ordination while in fuchsine the co-ordination appears to be through the two NH_2 groups attached to the phenyl rings which do not carry the $-CH_3$ group. Magnetic measurements shows the complexes to be diamagnetic as expected.

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Reaction of β-Diketonates of Nickel(II) with Thiocyanate and Azide Ions

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β-diketonates of Nickel(II) were reacted with potassium thiocyanate and sodium azide in 1 : 2 molar ratio in methanol medium and complexes having the general formula M_2 [Ni (β-dik)$_2$X$_2$] where M = K^+ or Na^+, H. β-dik = acetylacetone, benzoylacetone or dibenzoyl methane and X = SCN^- or N_3^- were isolated. I. R. study indicates that thiocyanate is coordinated to the metal ion through sulphur and the azide group through terminal nitrogen atom. The magnetic measurement and electronic spectral data reveal that complexes are octahedral. The molar conductance values indicate that the complexes are 1 : 2 electrolytes.

A large number of mixed ligand complexes of β-diketonates of nickel(II) with neutral hetero donor ligands have been reported[1-6]. Complexes of nickel(II) containing β-diketones and pseudohalides do not appear to have been studied earlier. Thiocyanate is an ambidentate group capable of bonding either through nitrogen or sulphur and ligand characterstics of azide group also have been well studied. It was therefore thought worthwhile to investigate the reaction of thiocyanate and azide ion with the β-diketonates of nickel(II) and to study the nature of their coordination around the central metal ion.

Experimental

All the chemicals used were of AR grade. The β-diketonates of nickel(II) were prepared by known methods. The thiocyanate and azide complexes were obtained by refluxing either the solution or suspensions of β-diketonates of nickel(II) in methanol with methanol solution of potassium thiocyanate or sodium azide in 1 : 2 molar ratio for a period of two to three hours. On cooling the resulting solution, solid products separated out, which were suction filtered, washed with absolute methanol, followed by ether and dried *in vacuo*.

Nickel and sulphur were estimated by standard methods. Electrical conductance was measured on M/1000 solutions either in acetone or pyridine using a Toshniwal conductivity bridge and a dip type cell. The magnetic susceptibility was determined at room temperature using Guoy method. The infrared absorption spectra were recorded on Nujol mulls using Unicam SP-200 double beam spectrophotometer. The electronic spectra in solution were recorded using Unicam SP-500 spectrophotometer. Colour, melting point, analytical, molar conductance and magnetic susceptibility data are given in Table-1. The infrared absorption bands pertaining to β-diketones, thiocyanate and azide groups and the electronic spectra are returned in Table 2.

Discussion

The compounds reported in this investigations have the general composition M_2[Ni (β-dik)$_2$X$_2$]. The thiocyanato compounds of bis acetylacetonate and benzoylacetonate are fairly soluble in acetone whereas the azido compounds and the thiocyanato compound of bis dibenzoyl methanate are only soluble in pyridine. The molar conductance values of the compounds in the respective solvents indicate them to be 2 : 1 electrolytes.

All the compounds are paramagnetic with μ_{eff} values ranging between 3.00 and 3.30 BM (Table 1) which are within the range for octahedral complexes of nickel(II) (2.83-3.40 BM)[7]. These compounds are therefore, spin-free, octahedral complexes involving the use of 4s $4p^3$ $4d^2$ hybrid orbitals for bonding.

Infrared spectra : By the introduction of an extra ligand to the structural assembly of the metal complex, the ν(C–C), ν(C–O) and ν(M–O) which are involved in a resonance system are expected to undergo shifts. In the present study, the ν(C–C) and ν(C–O) are shifted to lower frequencies as expected.

The thiocyanate group can be terminal N- or S-bonded or can function as a bridging group. The changes in ν(C–N)[8] and ν(C–S)[9] consequent to different modes of bonding have been discussed earlier. In the present compounds, ν(C–N) bands appear at ~2030 cm^{-1} and ν(C–S) bands appear at ~710 cm^{-1} (Table 2) indicating the presence of terminal S-bonded thiocyanate group.

The ionic KN_3 absorbs[10] at 2041 cm^{-1}(ν_{asy})

TABLE 1

ANALYTICAL, MELTING POINT, MOLAR CONDUCTANCE AND MAGNETIC SUSCEPTIBILITY DATA OF NICKEL(II) COMPLEXES.

Compound	Colour	M.P. (°C)	% Nickel Found	% Nickel Reqd.	% Sulphur Found	% Sulphur Reqd.	AM (mhos)	μ_{eff} (BM)
$K_2[Ni(acac)_2(SCN)_2]$	deep green	217 (d)	12.8	12.9	14.8	14.1	268	3.00
$Na_2[Ni(acac)_2(N_3)_2]$	light green	>250	15.2	15.0			128	3.00
$K_2[Ni(bzac)_2(SCN)_2]$	pea green	>250	9.4	10.1	11.3	11.1	254	3.30
$Na_2[Ni(bzac)_2(N_3)_2]$	green	>250	11.4	11.4			122	3.30
$K_2[Ni(bzbz)_2(SCN)_2]$	greenish yellow	>250	8.2	8.8	8.9	9.1	99	3.30
$Na_2[Ni(bzbz)_2(N_3)_2]$	bright green	>250	9.2	9.2			108	3.20

TABLE 2

INFRARED AND ELECTRONIC SPECTRAL DATA OF NICKEL(II) COMPLEXES IN CM^{-1}

Compound	β-diketone $\nu(C-C)$	β-diketone $\nu(C-O)$	Thiocyanate $\nu(C-N)$	Thiocyanate $\nu(C-S)$	Azide ν_{asy}	Azide ν_{sym}	Electronic spectra (ν_{max}) ν_1	Electronic spectra (ν_{max}) ν_2
KSCN			1963	749				
NaN_3					2041	1344		
$Ni(acac)_2(H_2O)_2$	1628	1553					<10,000	15,389
$Ni(bzac)_2(H_2O)_2$	1613	1555					<10,000	16,395
$Ni(bzbz)_2(H_2O)_2$	1625	1555					<10,000	16,425
$K_2[Ni(acac)_2(SCN)_2]$	1600	1520	2030	710			10,520	17,240
$Na_2[Ni(acac)_2(N_3)_2]$	1600	1525			2080	1260	10,526	17,860
$K_2[Ni(bzac)_2(SCN)_2]$	1590	1512	2030	708			10,810	17 240
$Na_2[Ni(bzac)_2(N_3)_2]$	1600	1525			2045	1275	10,765	17 860
$K_2[Ni(bzbz)_2(SCN)_2]$	1605	1530	2060	706			11,110	16,000
$Na_2[Ni(bzbz)_2(N_3)_2]$	1600	1540			2035	1270	10,265	18,180

and 1344 cm^{-1} (ν_{sym}). The shifts in these two frequencies on coordination were reported and discussed earlier[11,12]. In the compounds under report, the strong bands observed for ν_{sym} and ν_{asym} are in accordance with the earlier observations.

Electronic Spectra : For an octahedral nickel (II) complex three main bands are expected[5], ν_1, 8000 – 13,000; ν_2 14,000-19,000 and ν_3, 25,000-30,000 cm^{-1} arising from ${}^3A_{2g} \rightarrow {}^3T_{2g}$ (F), $\rightarrow {}^3T_{1g}$ (F) and ${}^3T_{1g}$ (P) transitions. In the present study the third band (ν_3) is obscured by the intense charge transfer bands. The bands noticed at 10,000 – 11,000 (ν_1) and 16,000 - 18,000 cm^{-1} (ν_2) may be assigned to ${}^3A_{2g} \rightarrow {}^3T_{2g}$ (F) and ${}^3A_{2g} \rightarrow {}^3T_{1g}$ transitions. Besides, very weak bands also appear at ~11,000, ~12,000, ~13,800, ~14,810 and ~19,230 cm^{-1} due to tetragonal distortion. Rowley and Drago[13] have also assigned similiar weak bands, to transition arising in molecules when passing from O_h to D_{4h} symmetry.

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Metal Complexes of Dithiodiglycollic Acid and Its Use as New Analytical Reagent for the Amperometric Determination of Ce(IV), Fe(III), Hg(II) and Hg(I)

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Amperometric titrations of Ce(IV), Fe(III), Hg(I) and Hg(II) at an applied potential of 0.0V, −0.6V, −0.5V and −0.55V respectively using dropping mercury indicator electrode, against dithiodiglycollic acid have been carried out. Solutions containing as little as 10 ppm of metal ion can be accurately determined with an error of ±0.5%. The metal complexes could be isolated in the solid forms and the combining ratio was also determined from their chemical analysis and their structures were confirmed from their i.r. spectra and magnetic measurements.

SURVEY of the existing literature revealed that nothing has so far been done on the metal complexes of dithiodiglycollic acid. The present communication deals with the amperometric determination of Ce(IV), Fe(III), Hg(II) and Hg(I) using dithiodiglycollic acid and the composition and structure of the reaction products formed on mixing the reactants in aqueous solutions.

Experimental

Physical measurements : as previously reported[1]

Reagents and solutions : The solutions of ferric nitrate, mercuric chloride, potassium nitrate, potassium hydroxide, dithiodiglycollic acid (Evans, U.S.A.) in double distilled water, ceric ammonium nitrate in 0.5 *N* sulphuric acid and mercurous nitrate in dilute nitric acid were prepared. All the reagents were of A.R. quality.

Results and Discussion

The pK_1 and pK_2 of the dithiodiglycollic acid as determined by potentiometric half titration method[2] (20 ml. of 0.0033 *M* reagent vs 0.1 *M* KOH) were 3.20 and 10.64 1 : 2 (M : L) stoichiometry of Fe(III) complex and 1 : 1 of Ce(IV), Hg(II) and Hg(I) complex was found in the concentration range from 0.00083 *M* to 0.0033 *M* by amperometric titrations carried out at −0.6 V and 0.0 V, −0.55 V and −0.5 V respectively.

Procedure for the determination : A measured volume of standard metal solution, to give the desired concentration, was introduced into a 100 ml. flask ; to this was added 50 ml. of *1M* KNO_3 and the solution diluted to the mark with the solvent. An aliquot (20 ml.) of this solution was transferred to a polarographic cell, deaerated by bubbling pure nitrogen and a potential of 0.0V, −0.6V, −0.55V and −0.5V in the determination of Ce(IV), Fe(III), Hg(II) and Hg(I) respectively vs SCE was applied, using as an indicator electrode. The *pH* of the solution was adjusted between 1.0 and 2.0, 2.5 and 4.0, 5.0 and 6.0 and 1.0 and 2.5 by the addition of HNO_3 or KOH in the case of (Ce(IV), Fe(III), Hg(II) and Hg(I) respectively. Measured volumes of the reagent solution were added and after each addition, the solution was stirred by bubbling nitrogen gas and the current measured after an interval of few minutes untill the precipitates formed were settled.

Solution containing as little as 140 ppm of metal ion be accurately determined and from 10 ppm to 140 ppm of the metal ion can be determined with an accuracy of ±0.5%.

To know the polarographic reduction behaviour of the ligand, a polarogram of the solution of dithiodiglycollic acid (0.0022*M*) containing potassium nitrate (0.5*M*) as supporting electrolyte and gelatin (0.003%) as maxima suppressor, was taken which indicated the presence of two waves. The half wave potential ($E_{1/2}$) and diffusion current (id) of the first wave was found to be −0.7V and 29.25 μA and of second wave −1.3V and 10.5 μA respectively. The plateau of the first wave (complete diffusion) was found beyond −1.0V and of second wave beyond −1.5V.

Interferences : Interference studies were carried out by taking an aliquot of the metal solution, adding 5-10 fold excess of the foreign ion and titrating as described above. Li(I), Na(I), K(I), Rb(I), Tl(I), Mg(II), Ca(II), Sr(II), Ba(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Pd(II), Pb(II), Cd(II), Mn(II), Sn(II), Al(III), Cr(III), As(III), Sb(III), Bi(III), In(III), Ga(III), Ir(III), Au(III), Sn(IV), Pt(IV), rare earth

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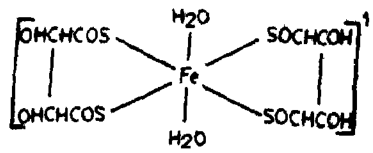
metal ions in trivalent state do not interfere while traces of Th(IV), Mo(VI) and W(VI) interefere. The presence of halide ions (Cl^-, Br^-, I^-) do not interfere in the estimation of Ce(IV), Fe(III) and Hg(II) but seriously interfere in the estimation of Hg(I).

The estimation of one metal out of these four is also interfered by the presence of other three metal ions.

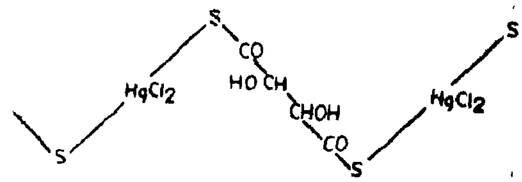
Preparation of the complexes and their magnetic and i.r. studies : The metal complexes were prepared by mixing the reactants containing a little excess of the ligand over the calculated amount in order to get a 1 : 1 (M : L) complex of Ce(IV), Hg(II) and Hg(I) and 1 : 2 complex of Fe(III). The white precipitates were formed in all the cases except of Fe(III) in which the precipitates were of yellow colour. These were filtered, washed several times with distilled water and then dried in a desiccator over anhydrous sulphuric acid. The results of chemical analysis are given in table 1. The first and second complex on treatment with *1M* NaCl gave the protons which were titrated *p*H-metrically with standard KOH.

The complexes of Ce(IV), Hg(II) and Hg(I) were diamagnetic in character while the complex of Fe(III) was paramagnetic with a magnetic moment of 5.1 B.M.

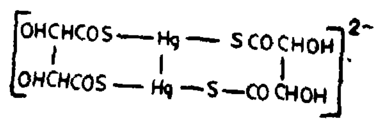
mode of coordinated water[3] were observed at 660 cm^{-1} and 820 cm^{-1} in the spectrum of Fe(III) complex. On the basis of above observations, the following structures may be proposed for the complexes.



(1)



(2)



(3)

TABLE 1—ANALYTICAL DATA OF THE COMPLEXES

Complexes	% Calc. M	% Calc. C	% Calc. S	% Found M	% Found C	% Found S
1. $H[Fe(C_4H_4O_4S_2)_2(H_2O)_2]$*	12.88	21.19	28.26	12.28	21.05	28.08
2. $H_2[Hg_2(C_4H_4O_4S_2)_2]$**	85.65	17.03	22.75	85.88	16.87	22.49
3. $H_2[Hg(C_4H_4O_4S_2)Cl_2]$***	44.41	10.62	14.17	44.09	10.54	14.00
4. $Ce(C_4H_4O_4S_2)(NO_3)_2$	31.54	10.58	14.41	31.27	10.49	14.18

*Hydrogen ion conc. = 2.2 meq./gm.
**Hydrogen ion conc. = 3.5 meq./gm.
***% of Cl [Calc ; 15.72% ; Found, 15.64%]

The i.r. spectra of the ligand and metal complexes gave the following information. A broad band obtained at 3000 cm^{-1} in the spectrum of the ligand due to $-OH$ was shifted to 3400 cm^{-1} in the spectra of complexes. The band due to $-C=O$ obtained at 1700 cm^{-1} in the spectrum of the ligand was shifted to 1600 cm^{-1}, 1580 cm^{-1}, 1570 cm^{-1} and 1540 cm^{-1} in the spectrum of Fe(III), Hg(II), Hg(I) and Ce(IV) complexes respectively which may be due to the mass effect. The bands due to $-SH$ at 2540 cm^{-1} in the ligand disappeared and at 450 cm^{-1} in the lower region shifted to 380 cm^{-1} in the spectra of complexes. This indicated the co-ordination of metal through sulphur.

Two extra bands due to wagging and rocking

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Stereochemical Features of Some Ni(II) and Co(II) Complexes of N-2, 5-Dihydroxy Acetophenacylidene Anthranilic Acid

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Nickel(II) and Cobalt(II) Complexes of the Composition $H_2[M(L)_2]$ and $H[M(L)X(H_2O)_2]$ [L = N-2, 5-dihydroxyacetophenacylideneanthranilic acid, X = Br] have been isolated and characterised by elemental analyses, magnetic, conductometric, electronic and i.r. spectral studies. Electronic spectral studies indicate that the latter type of complexes are tetragonally distorted from their regular cubic symmetry and it has been concluded that this distortion is produced due to unequal donor strengths of H_2O ligand. A possible correlation of it has been sought with the low values of magnetic moments observed in the complexes. I.R. spectral studies show that the metals are co-ordinated through the nitrogen of azomethine group, oxygens of carboxylic and phenolic groups. The entrance of water molecules within the co-ordination sphere is also supported by i.r. spectral studies.

SCHIFF Bases are very good chelating agents and their complexes with transition metals have recently been studied by workers[1-4]. N-2, 5-dihydroxyacetophenacylideneanthranilic acid (abbreviated as H_3-DAPAA) is capable of chelation by means of nitrogen atom of azomethine and oxygen atoms of carboxylic and phenolic groups. It was therefore decided to isolate a variety of Ni(II) and Co(II) complexes of H_3-DAPAA with common anions in nonaqueous media and investigate the possible bonding through i.r. spectral studies. We have also demonstrated the effect of distortion from the regular octahedral structure produced by H_2O ligand of unequal donor strength on the electronic spectra of complexes.

Experimental

N-2, 5-dihydroxyacetophenacylideneanthranilic acid was prepared by refluxing equimolar quantities of 2, 5-dihydroxyacetophenone and anthranilic acid in ethanol for 4.5 hrs. The contents were cooled, filtered and the product was washed with solvent ether (b.p. 60-80°). It was purified by crystallising from ethanol and its 80 per cent solution was used throughout.

Preparation and isolation of complexes

(a) *Dihydrogen-bis-(N-2, 5-dihydroxyacetophenacylideneanthranilic acido) Ni(II)*

A yellow-ochre solution was obtained by adding 7.5 ml of 0.02*M* ethanolic solution of nickel chloride to 30.0 ml of an equimolar solution of H_3-DAPAA at *p*H ~ 4.0. The reaction mixture was refluxed on steambath for 3.5 hrs. and the contents were cooled and kept in a refrigerator for two days, when yellowish green crystals were settled. The crystals were washed with water, ethanol and finally with ether and dried in vacuum at room temperature (yield 80 per cent). Anal. Calcd. for $H_2[Ni(C_{15}H_{11}NO_4)_2]$: C, 60.10 ; H, 4.0 ; N, 4.66 ; Ni, 9.84 per cent. Found : C, 59.85 ; H, 3.80 ; N, 4.54 ; Ni, 9.76 per cent.

(b) *Monobromo-monohydrogen-mono-(N-2, 5-dihydroxyacetophenacylideneanthranilic acido) diaquo Ni(II)*

A yellow coloured solution was obtained by mixing equimolar 50 per cent ethanolic solutions of nickel bromide and the ligand in the stoichiometric ratio (1 : 1). The reaction mixture was concentrated and the concentrate was kept in a refrigerator for few days, when yellow coloured crystals were separated out (yield 70 per cent). It is soluble in DMF, DMSO, nitromethane, nitrobenzene and benzene. Anal. Calcd. for $H[Ni(C_{15}H_{11}NO_4) Br(H_2O)_2]$: C, 45.03 ; H, 3.75 ; N, 3.50 ; Br, 20.01 ; Ni, 14.69 per cent. Found : C, 44.88 ; H, 3.52 ; N, 3.20 ; Br, 19.65 ; Ni, 14.54 per cent.

(c) *Dihydrogen-bis-(N-2, 5-dihydroxyacetophenacylideneanthranilic acido) Co(II)*

25 ml of 0.03M acetonic solution of cobalt chloride were mixed with 50 ml of equimolar acetonic solution of the ligand. The reaction mixture was placed in vacuum desicator over fused calcium chloride and concentrated by evaporation. The concentrate was cooled in refrigerator for few days, red coloured crystals were deposited which were washed successively with water, ethanol and ether and dried in vacuum. The complex compound is soluble in DMF, benzene, acetone, nitromethane (NM) and dimethylsulphoxide (DMSO). Anal. Calcd. for $H_2[Co(C_{15}H_{11}NO_4)_2]$; C, 60.10 ; H, 4.0 ; N, 4.67 ; Co, 9.83 per cent. Found : C, 59.88 ; H, 3.88 ; N, 4.52 ; Co, 9.67 per cent.

(d) *Monohydrogen-monobromo-mono-(N-2, 5-dihydroxyacetophenacylideneanthranilic acido) diaquo Co (II)*

Equimolar 75 per cent ethanolic solutions (0.02*M*) of Cobalt(II) bromide and the ligand were mixed in stoichiometric ratio (1 : 1). The contents were refluxed on waterbath for 2.5 hrs and cooled, when brown-green coloured crystals of the complex separated out. The crystals were washed with water and ethanol and dried, yield 85 per cent. It is soluble in DMF, NM, DMSO and benzene. Anal. Calcd. for $H[Co(C_{16}H_{11}NO_4)\ Br(H_2O)_2]$: C, 45.0 ; H, 3.80 ; N, 3.50 ; Br, 20.01 ; Co, 14.70 per cent. Found : C, 44.62 ; H, 3.61 ; N, 3.38 ; Br, 19.20 ; Co, 14.35 per cent.

Presence of hydrogen ions in the complexes was shown as reported previously.[5]

Analyses and apparatus

The microanalyses of carbon, hydrogen, nitrogen and halogens were performed by Mr. A.H. Siddiqui, Indian Institute of Technology, Kanpur-16, India. The conductometric, magnetic, electronic and i. r. spectral measurements were made as reported previously.[4, 5] Table 1 represents the magnetic, thermal and conductivity data of the complexes. The ligand field parameters are cited in Table 2. Tentative assignments of the bands observed in the i.r. spectra of H_3-DAPAA and its complexes are given in Table 3.

TABLE 1 MAGNETIC MOMENT, THERMAL AND CONDUCTIVITY DATA

Compound	Temp. (°K)	$\chi_M \times 10^6$ (c.g.s units)	μ_{eff} (B.M)	M.P. (°C)	Λ_M (DMF)	Λ_M (NM)
$H_2[Ni(C_{16}H_{11}NO_4)_2]$ (a)	303	3683	3.0	200	142	156
$H[Ni(C_{16}H_{11}NO_4)\ Br\ (H_2O)_2]$ (b)	303	3665	2.70	310	80	75
$H_2[Co(C_{16}H_{11}NO_4)_2]$ (c)	303	10640	4.82	255	156	170
$H[Co(C_{16}H_{11}NO_4)\ Br\ (H_2O)_2]$ (d)	303	7138	4.12	286	85	90

Λ_M, molecular conductance in ohm^{-1} mole^{-1} cm^2 at 25°

TABLE 2 – ELECTRONIC SPECTRAL DATA AND LIGAND FIELD PARAMETERS OF Ni(II) AND Co(II) COMPLEXES (VALUES IN CM^{-1})

Compound	Observed bands and their assignments $^3A_{2g}(F) \rightarrow$ $^3T_{2g}(F)$ (ν_1)	$^3T_{1g}(F)$ (ν_2)	$^3T_{1g}(P)$ (ν_3)	Calculated band positions ν_2	ν_3	$[(\nu_3-\nu_2)$ calcd $(\nu_3-\nu_2)$ obs.]	ν_2/ν_1	B	Dt	$D_q(x, y)$	$D_q(z)$
$H_2[Ni(C_{16}H_{11}NO_4)_2]$	9000	15000	26500	14955	26545	90	1.66	966	–	–	–
$H[Ni(C_{16}H_{11}NO_4)\ Br\ (H_2O)_2]$	10300 12640	20000	30200	19100	32090	2790	1.83	1166	+193	1264	174
	$^4T_{1g}(F) \rightarrow$ $^4T_{2g}(F)$ (ν_1)	$^4A_{2g}(F)$ (ν_2)	$^4T_{1g}(P)$ (ν_3)	ν_2 ↓		10Dq	B		β		
$H_2[Co(C_{16}H_{11}NO_4)_2]$	9000	20000	25000	20900		10580	1097		0.98		
$H[Co(C_{16}H_{11}NO_4)\ Br\ (H_2O)_2]$	8300	17350	23650	17560		9500	786		0.81		

TABLE 3. INFAR-RED SPECTRAL DATA (VALUES IN cm^{-1})

Ligand	Complex (a)	Complex (b)	Complex (c)	Complex (d)	Tentative assignments
1630 (m)	1610 (m)	1620 (m)	1610 (m)	1620 (m)	C=O stretching
3000 (w)	3000 (w)	2990 (w)	3000 (w)	2990 (w)	C–H aromatic
1610 (s)	1600 (s)	1600 (s)	1600 (s)	1640 (s)	Aromatic phenyl ring
2820 (w)	2810 (w)	2800 (w)	2820 (w)	2880 (w)	–CH stretching in CH_3
1600 (s)	1490 (s)	1490 (s)	1550 (s)	1500 (s)	–C=N perturbed
3440 (sh)	3350 (sh)	3380 (sh)	3400 (sh)	3400 (sh)	–OH phenolic (Reactive)
3280 (s)	3280 (s)	3270 (s)	3275 (s)	3280 (s)	–OH phenolic (Unreactive)
2570 (w)	2490 (w)	2490 (w)	2500 (w)	2500 (w)	–OH carboxylic
—	478 (w)	475 (m)	460 (m)	470 (w)	(M–O)
—	500 (m)	490 (m)	500 (m)	515 (m)	(M–N)
—	—	350 (w)	—	360 (w)	(M–Br)
—	—	3300 (sh)	—	3325 (sh)	(H_2O) stretching

m=medium, w=weak, s=sharp and sh=shoulder.

Results And Discussion

Analytical results show 1 : 1 and 1 : 2 metal to ligand stoichiometric ratio for Ni(II) and Co(II) complexes. The complexes were insoluble in water but soluble in DMF, DMSO, nitrobenzene and nitromethane (NM). The complexes show uni-univalent and biunivalent electrolytic nature as revealed by the molecular conductance data 75-90 ohm^{-1} $mole^{-1}$ cm^2 and 142-170 ohm^{-1} $mole^{-1}$ cm^2 respectively[6,7]. The acidic nature of the complexes was noticed by neutralising with caustic soda, 1 and 2g equivalents were used for complete neutralisation of uni-univalent and biunivalent complexes respectively[5].

Ni(II) Complexes

Ni(II) having electronic configuration $3d^8$ should exhibit magnetic moment higher than that expected for two unpaired electrons in octahedral symmetry (2.80-3.42 B.M.). The magnetic moment value (3.0 B.M.) observed for the complex $H_2[Ni(C_{16}H_{11}NO_4)_2]$ is comparable with the assignment of octahedral configuration. If in case of Ni(II), symmetry is allowed to be lower than cubic and if low symmetry component is larger, then spin paired term may be found in the neighbourhood[8]. Recently Holt and others[9] have shown that some complexes of Ni(II) lie on broadline between spin-free and spin-paired behaviour. At low temperatures it reaches diamagnetism whilst as the temperature increases, the magnetic moment approaches the spin-free value. X-ray investigation[10,11] of paramagnetic (2. 58 B.M.) bis-(mesostilbenediamine) nickel(II) dichloroacetate, has shown that crystal of this complex consists of a mixture of paramagnetic octahedral molecules and diamagnetic planar molecules. The subnormal magnetic moment 2.70 B.M. observed for $H[Ni(C_{16}H_{11}NO_4)Br(H_2O)_2]$ complex may be assumed to be intermediate between that of the low spin state (0.5 B. M. due to residual paramagnetism) and the high spin state (2.8 – 3.82 B.M.). It appears that the energy difference between the singlet and triplet has become comparable with the thermal energy (kT). This has been possible due to the lowering of symmetry[12] from $O_h \rightarrow D_{4h}$. In octahedral complexes, the singlet state lies above triplet states. As the field along the Z-axis decreases, the triplet state comes closer to the singlet state, thus allowing partial thermal transition resulting in the decrease of magnetic moment.

In the electronic spectrum of the complex (a) three principal bands are observed in the region 9000 cm^{-1} (ν_1), 15000 cm^{-1} (ν_2) and 26500 cm^{-1} (ν_3) whereas the calculated bands are found in the neighbourhood 14955 cm^{-1} (ν_2) and 26545 cm^{-1} (ν_3) showing thereby octahedral symmetry. Further confirmation of O_h symmetry is done by the fact that the ratio ν_2/ν_1 and the value)[$(\nu_3 - \nu_2)$ caldd-$(\nu_3 - \nu_2)$ obs.] are similar to those as observed for octahedral complexes[4,6]

In the electronic spectrum of the complex (b) four bands have been observed at 10900 cm^{-1}, 12640 cm^{-1}, 20000 cm^{-1} and 30200 cm^{-1}. The latter two bands are characteristics of an octahedral complex whereas the first two bands may be a consequence of the splitting in the ν_1 band due to low symmetry of the ligand field or it may also be because of the spin-forbidden transition.

Careful examination of the first, third and fourth bands provides following evidences whtch suggest that it is not a spin-forbidden transition but low symmetry component of the ν_1 band.

(i) For O_h symmetry, the calculated and experimental values of ν_2 and ν_3 should be in close agreement[12]. These values are not in agreement for the complex (b), revealing thereby tetragonal distortion of O_h symmetry.

(ii) For d^8 complexes with O_h symmetry, Lever[13] observed that as 10 D_q increases, the configuration interaction between excited state T_{1g} (F) and T_{1g} (P) lowers the ratio ν_2/ν_1 from the theoretical value

1.8∼1.5-1.7. However the tetragonal distortion produces E-components of the T_{1g} (F) and T_{2g} levels and the subsequent interaction and repulsion between these levels would cause an increase in the ratio ν_2/ν_1. This ratio for the (b) complex is 1.83 which is greater than the usual range for octahedral complexes, characterising thereby the complex to be tetragonal.

(iii) The value $[(\nu_3-\nu_2)$ calcd.-$(\nu_3-\nu_2)$ obs.] comeout to be 90 (complex-a) and 2790 cm^{-1} (complex-b). The small value confirms O_h symmetry whereas the larger value for complex (b) has been taken as a measure of the tetragonal distortion[14].

(iv) Assuming O_h symmetry, the values of B calculated for these complexes from the diagonal sum rule come out to be 966 and 1166 cm^{-1}. The former value is lesser whilst the latter is greater than the free ion value (1080 cm^{-1}) showing thereby O_h symmetry for the complex (a) and distortion from regular cubic symmetry for the complex (b).

It has, therefore been, concluded that the band at 12640 cm^{-1} is the low symmetry component. Hence for D_{4h} symmetry with H_2O ligands co-ordinated along Z-axis, the most probable transitions for the first two bands would be $^3B_{1g}\rightarrow{}^3E_g$ (10900 cm^{-1}) and $^3B_{1g}\rightarrow{}^3B_{2g}$ (12640 cm^{-1}) having energies $10D_q-\frac{35}{4}$ Dt and $10D_q^E$ in terms of radial parameters. The value of parameter Dt, which is directly related to the tetragonal distortion along the Z-axis, has been calculated to be 193 cm^{-1} for the complex (b). It is evident from the calculated values of $D_q(x,y)$, 1264 cm^{-1} and $D_q(z)$, 174 cm^{-1} that the field along the Z-axis is much weaker than along the xy plane, supporting thereby the lowering in the magnetic moment value observed for the complex (b)

Cobalt (II) Complexes

The hexa-co-ordinated complexes of Co(II) ion (d^7) would be high-spin at the weak field limit and low-spin at the strong field, while these states are expected to have comparable stable states somewhere between the two extremes within a comparatively small range of field strength[15]. The magnetic moment value for the complex (c) is comparable with that of high-spin octahedral complexes and for the complex (d) it lies in between the values of low and high-spin octahedral cobaltous complexes which may be explained as follows.

The analytical and electronic spectral data do not show the presence of any Co(III) admixed with Co(II). The possibility of the polymeric structure can be ruled out on the basis of conductivity data. For the complex (d), the observed subnormal value of magnetic moment 4.12 B.M. may be because of the presence of lower symmetry component and partial covalent character.

The electronic spectra of complexes (c) and (d) show three bands at 9000, 8300 cm^{-1} [$^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)$ (ν_1)]; 20000, 17350 cm^{-1} [$^4T_{1g}(F)\rightarrow{}^4A_{2g}(F)$ (ν_2)] and 25000, 23650 cm^{-1} [$^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$ (ν_3)]. Calculated band positions ν_2 for the complexes (c) and (d) 20900 cm^{-1} and 17560 cm^{-1} show that experimental and calculated bands are comparable for the complex (d) whilst they differ markedly in the case of complex (c). It may be taken as a measure of low symmetry component[16] due to distortion for the complex (d). Using Figgis equations[17] the values of $10D_q$ and B were calculated to be 10530, 9500 and 1097, 786. Thus due to unequal donor strength of H_2O ligand, tetragonal distortion along X-axis is suggested for the complex (d). Agarwal and others[18,19] have also observed spectra similar to the present complex (d) in case of tetragonally distorted octahedral Co(II) complexes.

The values of nephelauxetic ratio arising out of partial overlap of 3d orbitals with the σ and π orbitals of surrounding donors consist of both $f^2\sigma$ and $f^2\pi$ i.e. $f^2=f^2\pi$. $f^2\sigma$ and are 0.98 and 0.81 for the complexes (c) and (d) respectively. The former value is comparable to that of octahedral Co(II) complexes[3] whereas the latter value is comparable to that of tetragonally distorted octahedral Co(II) complexes[20]. The partial covalent character may also be responsible for the subnormal value of magnetic moment in the complex (d) as pointed earlier[21-22].

Infrared spectral studies

In the i.r. spectra of metal chelates the stretching frequencies of azomethine $CH_3C=N$ (1600 cm^{-1}), phenolic-OH (3440 cm^{-1}) and carboxylic $-OH$ (2570 cm^{-1}) groups are lowered and bands around 1490-1550 cm^{-1}, 3350-3400 cm^{-1} and 2490-2500 cm^{-1} appear which show complex formation. This view is supported by the formation of M-N (490-515 cm^{-1}) and M-O (460-478 cm^{-1}) bonds. In the complexes (b) and (d) metal-halogen bond is also formed, it is revealed by the appearance of band around 350 cm^{-1}. The band around 3280 cm^{-1} indicates the presence of unreacted hydroxyl group. Co-ordination of water molecules is indicated by the appearance of bands at 3300 cm^{-1} and 3325 cm^{-1} in the complexes (b) and (d).

Details are given in Table 3.

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A Kinetic Study of the Reaction of Diethyl Phosphite with Mercuric Acetate

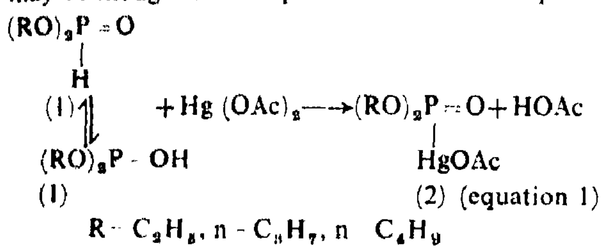
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Manuscript received 12 April 1977, accepted 29 July 1977

The reaction of diethyl phosphite with mercuric acetate to form the mercurated phosphorus compound (2) has been studied kinetically in dry benzene. A mechanism involving a nucleophilic attack of the phosphoryl oxygen on mercuric acetate, to give an intermediate phosphonium ion, is discussed.

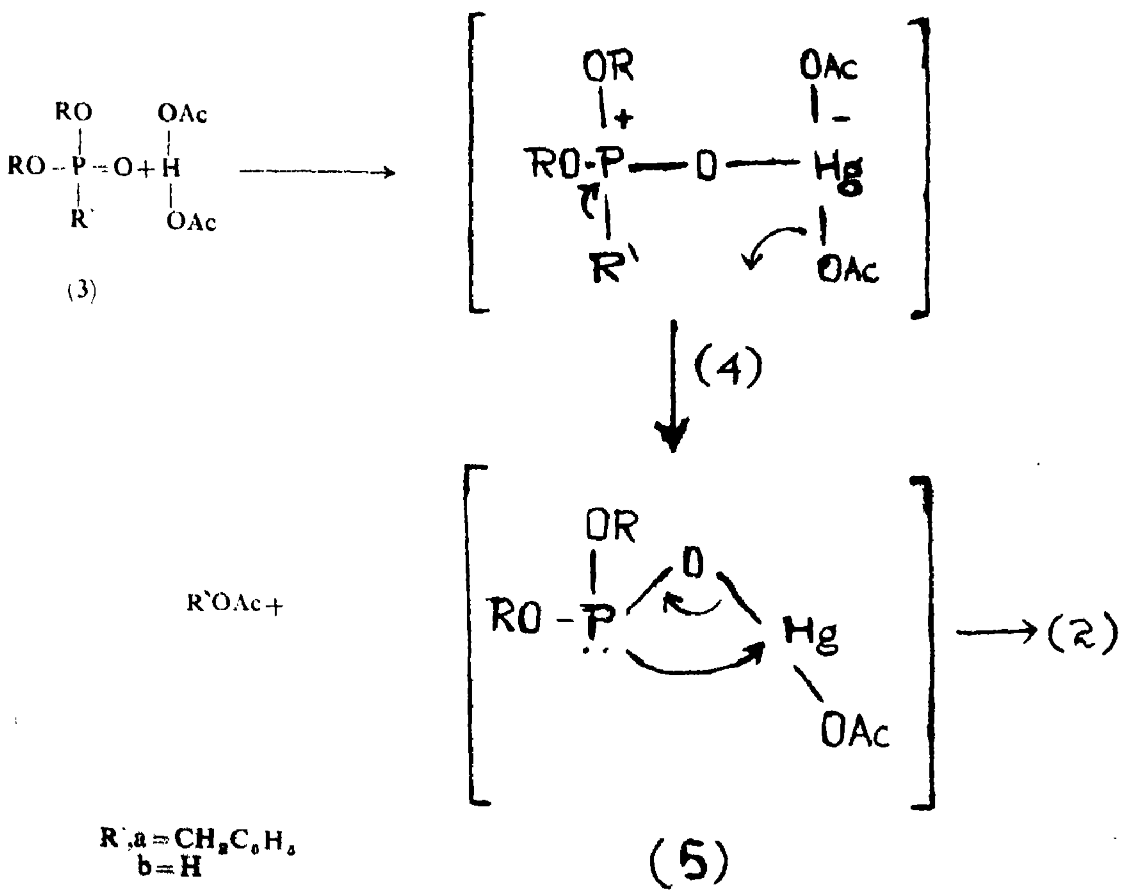
FOX and Venezky[1] reported that dialkyl phosphites (1) react with mercuric salts to give dialkyl phosphonylmercuric acetate (2). The reaction may be thought to take place via the nucleophilic



attack of the lone pair of electrons on the phosphorus atoms of (1) on the mercuric acetate.

If this is the case, replacement of (H) in (1) by a heavier group (e.g.. $-CH_2C_6H_5$) would compel the reaction with mercuric acetate to proceed in a different way and give another product.

However, we reported[2] that dialkyl benzylphosphonates (3a) react with mercuric acetate to give (2) at room temperature according to the following mechanism :



(Equation 2)

We believe that this mechanism (cf. equation 2) is also applicable to dialkyl phosphites with the liberation of acetic acid which facilitate the following up of the reaction rate by a simple titration.

The kinetic study of such a reaction would help in differentiation between the above mechanism and the probable mechanism including dissociation of dialkyl phosphite as follows :

$$(RO)_2\underset{\displaystyle H}{\underset{|}{P}}=O \underset{\text{in benzene}}{\overset{\text{slow}}{\rightleftharpoons}} (RO)_2\bar{P}=O+H^+ \qquad (6)$$

$$(RO)_2\overset{\displaystyle O}{\overset{\|}{P}}: +Hg(OAc)_2 \overset{\text{rapid}}{\rightleftharpoons} (RO)_2\overset{\displaystyle O}{\overset{\|}{P}}-Hg-OAc + OAc^-$$

(equation 3)

Experimental

Materials :

Mercuric acetate is of reagent grade and was used as received from Matheson Colemen and Bell.

Diethyl phosphite was synthesized by the reaction of PCl_3 with absolute ethyl alcohol and rectified several times under reduced nitrogen pressure.[3] Solvents were purified by ordinary methods.[4]

Kinetic Procedures :

Mercuric acetate 1.274 g (0.004 mole) was weighed accurately in a glass-stoppered conical flask and placed in an ultrathermostated bath (±0.1°.) After ca. 20 min., 10 ml of the benzene solution of diethyl phosphite (0.004 mole) was poured in the conical flask which was shaken vigorously. The rate of the reaction was followed by titrating aliquots at different intervals against standardized sodium ethoxide solution in benzene using neutral red as indicator. A blank experiment was carried out without the addition of the phosphite. The experiment at each temperature was repeated three times.

Results and Discussion

Order of Reaction :

The reaction proved to be of the second-order as shown by using different initial concentrations of each reactant (mercuric acetate and diethyl phosphite). The k_2 values obtained from three experiments performed with different initial concentrations of each reactant, were found to be in fairly good agreement with the value obtained when using the same initial concentration of each reactant. Table 1 summarizes the kinetic data and k_2 is essentially invariant over the indicated range of concentration.

TABLE—1

RATES OF REACTION OF MERCURIC ACETATE WITH DIETHYL PHOSPHITE AT 5° IN BENZENE

$Hg(OAc)_2/M$	$(C_2H_5O)_2\overset{O}{\overset{\|}{P}}-H/M$	$10^2k,\ M^{-1}\ Sec^{-1}$
0.004	0.004	3.55
0.004	0.006	3.68
0.004	0.008	3.68
0.004	0.01	3.64

Temperature effect :

The rate of reaction was measured at various temperatures, viz, 5°, 10° and 15°. The results are summarized in Table 2.

TABLE—2

VALUES OF k_2 AS A FUNCTION OF TEMPERATURE

Temperature	$10^2k,\ M^{-1}\ Sec^{-1}$
5	3.55
10	5.00
15	7.50

The plot of log k vs. 1/T afforded a good straight line, which gave the values of 11.2 kcal mol^{-1} and −26.8 eu for the energy and entropy of activation respectively.

Discussion

Our postulated mechanism (equation 2), involves a nucleophilic attack of the phosphoryl oxygen of diethyl phosphite on murcuric acetate to give a phosphonium ion intermediate (4b).

Each molecule of diethyl phosphite and mercuric acetate should participate in the rate determining step. The large negative entropy of activation reflects a high degree of orientation and/or a rigid structure in the transition state, and this negative value is consistent with a reaction of neutral molecules via polarised transition states to yield ions.[5] Hence, this S_N2 mechanism supports that the reaction is likely to proceed via (equation 2, R' = H).

In the intermediate phosphonium ion (4b) an intramolecular nucleophilic attack of the acetate occurs on the proton to give acetic acid and a mercurated trivalent phosphorus compound (5). The latter compound rearranges in the reaction medium to give the final product (2). This reaction may proceed via a concerted three-center rearrangement of the phosphorus atom initiated by nucleophilic attack of the lone pair of electrons. The driving force for this rearrangement is the high stability of the (P=O) bond. This type of rearrangement may be considered as a special case of the known Arbusov

rearrangement.[6] The kinetic data excludes the mechanism proposed in equation (3) as it should be S_N1 in the phosphite only.

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Mechanism of Oxidation of Cyclohexanone by N-Bromosuccinimide

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Oxidation of cyclohexanone by acidic N-bromosuccinimide (NBS) was made in presence of mercuric acetate. A zero order dependence to NBS and a first order dependence to cyclohexanone and [H⁺] was observed. No significant effect of ionic strength, mercuric acetate or succinimide was evident. The effect of addition of methanol was positive. Formation of protonated cyclohexanone from the enol is shown to be slow and rate-determining step.

OXIDATION of cyclohexanone has been made using a wide variety of oxidising agents[1-9]. The present work incorporates systematic kinetic study of oxidation of cyclohexanone by acidic NBS in presence of mercuric acetate and a suitable mechanism is proposed. It is of interest that the literature on step by step mechanism of oxidation by NBS is scanty.

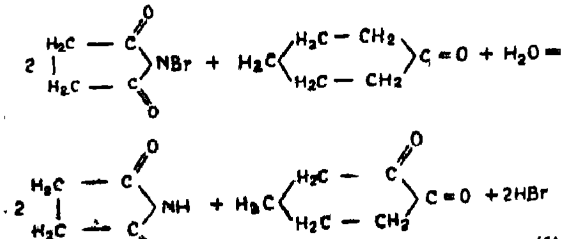
Experimental

Aqueous solutions of NBS were always prepared fresh in black coated flasks using G.R.S., Merck samples and their strengths were checked using iodometric method[10]. Mercuric acetate and succinimide were of E. Merck and H & W (England) grade. Cyclohexanone used was from E. Merck. All other reagents viz. sodium perchlorate, methanol, perchloric acid etc. were of analytical grade and triple distilled water was used throughout the course of investigations. The reaction stills were blackened from outside.

Kinetics were monitored by estimating unconsumed NBS iodometrically. The reactions were initiated by adding cyclohexanone to the mixture of NBS, perchloric acid and other reagents at constant temperature ($\pm 0.1°$).

Stoichiometry

Reaction mixtures containing known excess of NBS over cyclohexanone were allowed to equilibrate under experimental conditions. The results showed that one mole of cyclohexanone consumes two moles of NBS in accordance to stoichiometric equation (1).



... (1)

The product 1, 2-cyclohexanedione was confirmed by spot test[11]:

Results

The kinetic investigations were carried out at several initial concentration of the reactants. It was observed that neither mercuric acetate interferes with the liberated iodine nor the oxidation of cyclohexanone by mercuric acetate or iodine takes place under the experimental conditions. Further, there was no change in pH during any kinetic run. Concentration-time plots in NBS were found to be straight lines. Zero order rate constants (k_0) in NBS were thus obtained which showed a linear increase with increase in cyclohexanone concentration (Table 1). A linear increase in the zero order rate constant in NBS was observed with the increase in cyclohexanone concentration (Fig. 1). The average values of first order rate constants $k_1 = k_0/[\text{cyclohexanone}]$ were found as $(8.65 \pm 0.22) \times 10^{-5}$ and $(14.2 \pm 0.30) \times 10^{-5}$ sec^{-1} at 35° and 40° respectively.

TABLE—1

EFFECT OF REACTANTS' CONCENTRATION ON THE REACTION RATE

$[HClO_4] = 2.5 \times 10^{-2} M$ and $[Hg(OAc)_2] = 2.0 \times 10^{-3} M$

10^3 [NBS] M	10^2 [Cyclohexanone] M	$k_0 \times 10^7$ mol. l^{-1} sec^{-1} at 35°	40°
0.8	1.0	8.42	13.9
1.0	1.0	8.65	14.2
1.2	1.0	8.87	14.6
1.4	1.0	8.43	14.4
1.6	1.0	8.77	14.5
1.0	0.5	4.28	7.11
1.0	1.5	12.9	20.8
1.0	2.0	17.8	28.7
1.0	2.5	21.5	36.3

The effect of variation of ionic strength, mercuric acetate concentration, succinimide concentration, addition of methanol and a change in hydrogen ion

* To whom all correspondence should be made.

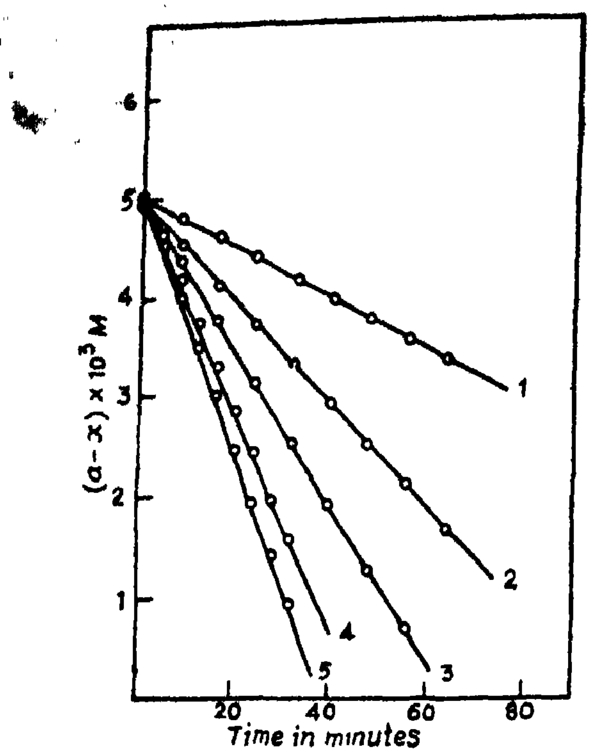


Fig. 1. Zero order rate plots at 35°
$[NBS] = 1.0 \times 10^{-3} M$, $[HClO_4] = 2.5 \times 10^{-3} M$
$[Hg(OAc)_2] = 2.0 \times 10^{-3} M$, [Cyclohexanone] = 0.5, 1.0, 1.5, 2.0 and $2.5 \times 10^{-3} M$ in 1, 2, 3, 4 and 5 respectively.

concentration was studied. An increase in hydrogen ion concentration increased the zero order rate constants linearly (Table 2) and the average value of $k_1' = k_0/[HClO_4]$ was found as (3.54 ± 0.18) and $(5.70 \pm 0.15) \times 10^{-5}$ sec^{-1} at 35° and 40° respectively.

TABLE—2
EFFECT OF $[H^+]$ ON THE REACTION RATE
$[NBS] = 1.0 \times 10^{-3} M$, [Cyclohexanone] $= 10^{-3} M$ and $[Hg(OAc)_2] = 2.0 \times 10^{-3} M$

10^3 $[HClO_4]$ M	$k_0 \times 10^7$ mol. l^{-1} sec^{-1} 35°	40°	$k'_1 = k_0/[HClO_4]$ sec^{-1} 35°	40°
2.0	7.27	11.7	3.69	5.85
2.5	8.65	14.2	3.46	5.68
3.0	10.1	17.1	3.36	5.70
4.0	14.9	22.2	3.72	5.55
5.0	17.7	28.7	3.54	5.74

Addition of $NaClO_4$ from nil to 1 *M* and mercuric acetate and succinimide from nil to 0.01 *M* showed no effect on the reaction rate. However, addition of methanol showed a positive influence on the reaction rate (Table 3).

TABLE—3
EFFECT OF METHANOL ON REACTION RATE AT 35°
$[NBS] = 1.0 \times 10^{-3} M$, [Cyclohexanone] $= 1.2 \times 10^{-3} M$, $[HClO_4] = 2.5 \times 10^{-3} M$ and $[Hg(OAc)_2] = 2.0 \times 10^{-3} M$

MeOH %	$k_0 \times 10^7$ mol. l^{-1} sec^{-1}
0	8.65
10	9.85
20	10.8
30	11.2
40	12.8

Various rate parameters viz. energy of activation ($\Delta E^{\neq}$), frequency factor (A), entropy of activation ($\Delta S^{\neq}$), heat of activation ($\Delta H^{\neq}$) and free energy of activation ($\Delta F^{\neq}$) were computed from the rate study measurement carried out at five different temperatures (30° – 50°) and the average values were found as 20.1 kcals mol^{-1}, $(5.40 \pm 0.11) \times 10^{11}$ l.mol^{-1} sec^{-1}, (-5.83 ± 0.03) e.u., 19.5 ± 0.1 kcals mol^{-1} and 21.4 ± 0.1 kcals mol^{-1} respectively.

Discussion

It is well known that NBS exists in acid media in following equilibria,

$$NBS + H^+ \rightleftharpoons M + Br^+ \quad (M = \text{succinimide}) \qquad (2)$$

$$NBS + H^+ \rightleftharpoons NBSH^+ \qquad (3)$$

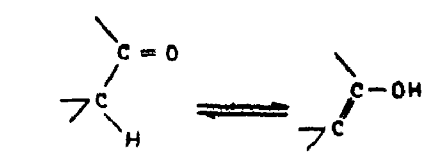
and thus the oxidising species could be either NBS itself or Br^+ [12,13] or $NBSH^+$ [14].

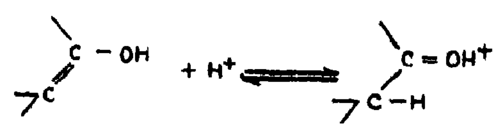
NBS forms free bromine by interaction with HBr,

$$NBS + HBr \longrightarrow M + Br_2 \qquad (4)$$

However in presence of mercuric acetate Br^- is fixed up as $HgBr_4^{2-}$ or unionised $HgBr_2$ [15,16]. Thus in the present studies any oxidation by free bromine is completely excluded.

It is seen that the order in NBS is zero and according to Littler[8] in such a case with 2-electron oxidants, the rates of oxidation are related to rates of enolisation. The acid catalysed oxidation of ketone clearly points out to the fact that the protonated form of the ketone is involved in the oxidation process. The accepted mechanism of formation of the protonated enol is as follows,


(5)


(6)

This protonated enol formed in step (6) reacts with any of the species derived from NBS viz. NBS, Br^+ or $NBSH^+$ in fast steps to give the final product.

Summarising,

$$S+H^{+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH^{+} \quad \ldots\ldots \quad \text{slow} \qquad (7)$$

$$SH^{+}+NBS \xrightarrow{k_2} X^{+}+M \quad \ldots\ldots \text{ fast} \qquad (8)$$

$$X^{+}+NBS \xrightarrow{k_3} \text{Products} \quad \ldots\ldots \quad \text{fast} \qquad (9)$$

where X^+ represents the intermediate complex.

As the steps (8) and (9) are much faster in comparison to (7), it is difficult to argue about the relative merits of NBS species taking part in these steps. But, still, the balance lies more in favour of NBS itself rather than $NBSH^+$ or Br^+ as the reaction of SH^+ and Br^+ or $NBSH^+$ (step 8) would be a reaction between two positive charged ions and may not be faster in comparison to (7) as suggested.

The proposed mechanism gives rise to the following rate law,

$$-\frac{d}{dt}[NBS]=2k_1\ [S]\ [H^+] \qquad (10)$$

which is consistent with the observed kinetics. The observed positive effect of methanol agrees well for a rate-determining reaction between a positive ion and a dipole. The average value of specific rate constant $k_s=k_0/[H^+]\ [S]$ has been obtained as $(3.46\pm0.11)\times10^{-3}$ l. mole^{-1} sec^{-1} at 35°.

Thus it is clear that NBS oxidation of cyclohexanone involves the formation of protonated enol in a slow and rate determining step, which is subsequently oxidised by NBS to products in fast steps.

Acknowledgements

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Synthesis of New 2 : 6 Bis Substituted Glycyl and Phenoxy Acetyl Benzo[1,2-d ; 4, 5-d] Bisoxazole

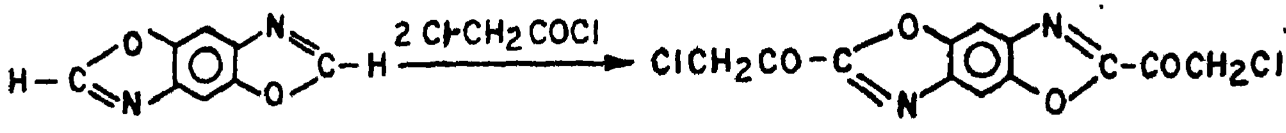
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Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt.

The parent benzo [1, 2-d ; 4, 5-d] bisoxazole 1 react with chloroacetyl chloride giving 2 : 6 bischloroacetyl [benzdioxazole 2 which interacts readily with amines and hydrazine. The bis hydrazinoacetyl benzdioxazole 4 on condensation with aldehydes give new schiff bases. 5. 1 also reacted with phthalyl amino acid chloride, or with phenoxy acetyl chloride giving the corresponding bisphthalimido acyl benzdioxazole 6, and bis phenoxy acetyl benzdioxazole 8 respectively.

BENZOXAZOLE and other condensed oxazoles find wide application in different industrial and biological aspects[1,2,3].

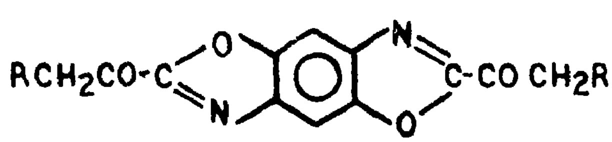
In the present investigation and in continuity with previous work[4,5] attempts were made to prepare different 2 : 6 benzdioxazole derivatives from the parent benzo [1, 2-d ; 4, 5-d] bisoxazole[6]. 1. Thus when 1 reacted with chloroacetyl chloride in dry toluene gave 2 : 6 bis chloroacetyl benzdioxazole 2 in good yield.



1 2

2 Reacted readily[7] with secondary amines, morphine, piperidine, ephedrine, phenothiazine and anisidine in toluene giving the corresponding 2 : 6 bis glycyl benzdioxazole 3_{a-e}.

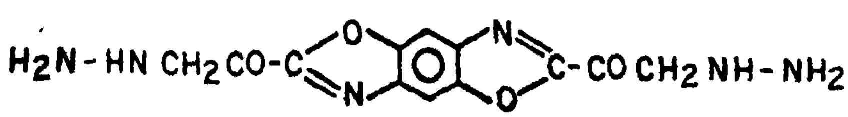
The structures of 3 have been established by their analytical data and their IR spectra (C=O ; 1700 - 1685 cm^{-1})[10].



3

3	R
a –	morphilino
b –	piperidino
c –	ephedrino
d –	phenothiazino
e –	anisidino

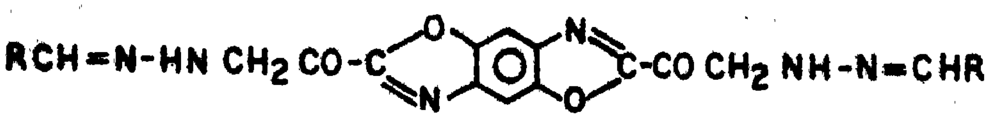
Condensation of one mole of 2 with two moles of hydrazine hydrate furnished 2 : 6 bis hydrazinoacetyl benzdioxazole 4.



4

The IR spectrum of this compound showed absorption bands at 1700 cm^{-1} (C=O) group and 3380 cm^{-1} (NH) group [10].

The structure of compounds 8 was established from the following: (i) correct analytical data, (ii) infrared absorption spectra which showed intense absorption bands corresponding to C=O groups[10] at about 1700-1670 cm^{-1}, and phenolic –C–O vibration band near 1280 cm^{-1}.



5

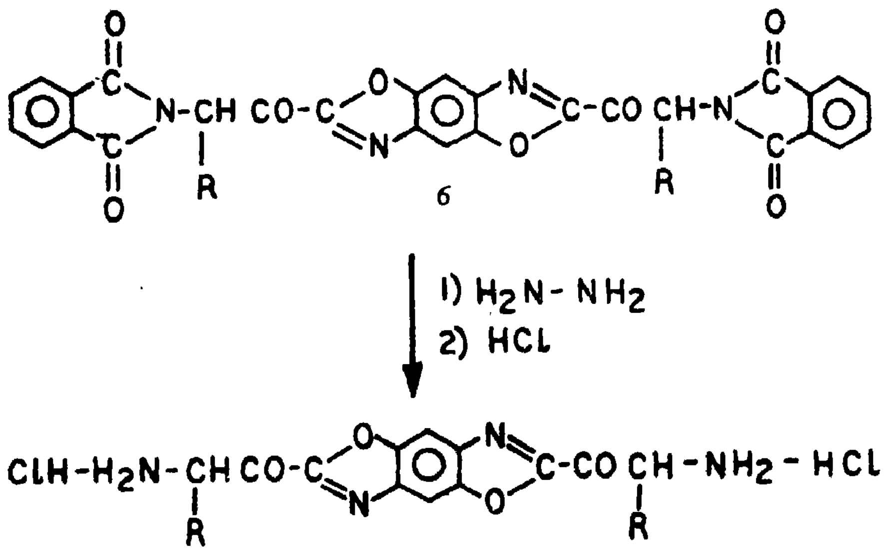
5	R
a –	C_6H_5
b –	$P-CH_3O-C_6H_4-$
c –	$O-OH.C_6H_4-$
d –	$P(CH_3)_2N.C_6H_4-$
e –	$P-NO_2-C_6H_4$
f –	$P-OH-C_6H_4$

Condensation of 4 with aldehydes in glacial acetic acid furnished the schiff bases 5.

The structures of these compounds were established by their analytical data and IR spectral data which showed absorption bands at 1620 cm^{-1} (C=N), 1695 cm^{-1} (C=O) and 3350 cm^{-1} (NH) stretching frequency[10].

Experimental

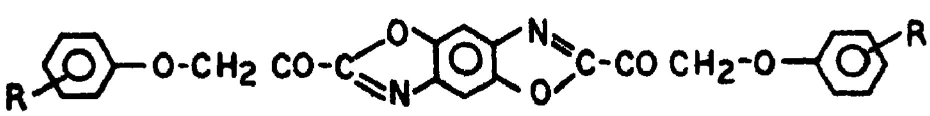
Infrared spectra were determined in KBr pellets on unicam sp 200 G infrared spectrophotometer. All melting points are uncorrected.



6

7

6, 7	R
a	H
b	CH_3-
c	$(CH_3)_2CH-$
d	$(CH_3)_2CH_2CH$



8

8	R
a	$P-NO_2$
b	$P-Cl$
c	$O-NO_2$
d	$O-Cl$

2 Reacted also with phthalyl amino acid chlorides[8] in dioxane and in presence of triethylamine as a catalyst to give quantitative yield of 2 : 6 bis phthalimide acyl-benzdioxazole 6. The phthalyl group of the latter 6 was removed by hydrazinolysis to give bis glycyl benzdioxazole 7.

Reaction of 2 with phenoxyacetyl chloride[9] in dioxane and in presence of triethylamine furnished 2 : 6 bis phenoxyacetyl benzdioxazole 8.

The parent benzdioxazole[6] 1, phthalyl amino acid chloride[8], and phenoxy acetyl chlorides[9] were prepared by the known methods.

2 : 6 bis-chloroacetyl benzdioxazole 2

Chloroacetylchloride (0.02 mol) was added slowly to benzdioxazole (0.01 mol) in dry toluene (150 ml) and the reaction mixture refluxed for 3 hrs. Toluene was removed under reduced pressure, the residue was filtered off and then crystallized from alcohol. Yield 83%, m.p. 102-3°.

$C_{12}H_6N_2O_4Cl_2$ (313) Calcd. C 46.01 H 2.91 N 8.94
Found. C 46.24 H 2.02 N 9.09

2 : 6 bis glycyl benzdioxazole derivatives 3 (a-e)

A mixture of 2 (0.01 mol) and the appropriate base (0.02 mol) in 20 ml of dry toluene was refluxed for 3 hours. The amine hydrochloride was filtered off, the organic layer extracted with 1*N* HCl (3 × 30 ml), and the acidic extract neutralized with sodium carbonate solution. The precipitated solid was collected, washed with sodium carbonate solution and then crystallized from alcohol-benzene mixture to give 3_{a-e}.

Table 1 represents the physical and analytical data of the compounds 3_{a-e}.

TABLE 1

Comp. 3 No.	Yield	m.p. °C	Formula (Mol. Wt)	Found/Calcd %C	%H	%N
a	65	136-7	$C_{20}H_{22}O_6N_4$ (414)	58.21 58.00	5.45 5.31	13.60 13.52
b	70	159-60	$C_{22}H_{26}N_4O_4$ (410)	64.51 64.39	6.41 6.34	13.74 13.61
c	67	170	$C_{32}H_{34}N_4O_6$ (570)	67.55 67.36	6.14 6.00	9.91 9.82
d	69	193-5	$C_{36}H_{22}N_4S_2O_4$ (638)	61.82 61.70	3.55 3.47	8.81 8.78
e	70	201-3	$C_{26}H_{22}N_4O_6$ (486)	64.30 64.19	4.61 4.52	11.60 11.52

2 : 6 bis hydrazinoacetyl benzdioxazole 4

A mixture of 2 (0.01 mol) and hydrazine hydrate (99-100% ; 0.02 mol) in 15 ml of ethanol was refluxed for 3 hrs. The reaction mixture was allowed to cool, diluted with water and crystallized from ethanol-water to give pale-yellow needles of 4 in 70% yield, m.p. 210-12° ;

$C_{10}H_{12}N_6O_4$ (304) Calcd. C 47.36 H 3.94 N 27.63
Found. C 47.51 H 3.98 N 27.71

Preparation of Schiff's bases 5_{a-f}.

A solution of 4 (1 mol) and the appropriate aldehyde (2 mol) in glacial acetic acid was refluxed for 2-3 hrs.

The reaction mixture was cooled, poured onto crushed ice and the deposited solid was collected, washed several times with cold water and then crystallized from alcohol to give pale-green products of 5_{a-f}.

Table 2 represents the physical and analytical data of 5.

Preparation of bis phthalimido acyl benzdioxazole derivatives 6

To (0.1 mol) of 1 in dioxane (10 ml), (0.2 mol) of N-phthalyl amino acid chloride in dioxane (5 ml) was added followed by (0.2 mol) of triethylamine, and then allowed to stand overnight at room temperature. The reaction mixture was treated with 2*N* HCl, and the precipitated solid was filtered, and recrystallized from ethyl acetate.

TABLE 2

Comp. 5 No.	Yield %	m.p. °C	Formula (Mol. Wt)	Found/Calcd. %C	%H	%N
a	70	180-2	$C_{26}H_{20}N_6O_4$ (480)	65.19 65.00	4.30 4.16	17.61 16.50
b	72	219-20	$C_{28}H_{24}N_6O_6$ (540)	62.35 62.22	4.61 4.44	15.70 15.55
c	75	231-3	$C_{26}H_{20}N_6O_6$ (512)	61.02 60.93	3.98 3.90	16.52 16.40
d	72	203-5	$C_{30}H_{30}N_8O_4$ (566)	63.71 63.60	5.33 5.30	19.90 19.78
e	71	228-30	$C_{26}H_{18}N_8O_8$ (570)	54.82 54.70	3.31 3.15	19.80 19.64
f	78	240-2	$C_{26}H_{20}N_6O_6$ (512)	61.05 60.93	4.01 3.90	16.58 16.40

Table 3 represents the physical and analytical data of 6.

TABLE 3

Comp. 6 No.	Yield %	m.p. °C	Formula (Mol.Wt)	Found/Calcd. %C	%H	%N
a	80	156-8	$C_{29}H_{14}N_4O_9$ (534)	63.07 62.92	2.81 2.62	10.68 10.50
b	83	169-71	$C_{30}H_{18}N_4O_8$ (562)	64.18 64.05	3.31 3.20	10.05 9.96
c	80	187-9	$C_{34}H_{26}N_4O_8$ (618)	66.18 66.02	4.31 4.20	9.21 9.06
d	81	206-8	$C_{36}H_{30}N_4O_8$ (646)	66.98 66.87	4.81 4.64	8.78 8.66

Preparation of bis glycyl benzdioxazole hydrochloride 7

A mixture of 6 (0.5 g) in ethanol (30 ml), and hydrazine hydrate (10 ml) was refluxed for 1 hour. The reaction mixture was evaporated till dryness, the residue was warmed at 50° for 10 minutes with 25 ml of 2*N* HCl and allowed to stand at room temperature for 1/2 hrs. The precipitated phthalic hydrazide was filtered, the filtrate was evaporated under vacuum to give compounds 7 and recrystallized from ethylacetate. Table 4 represents the physical and analytical data of 7.

TABLE 4

Comp. 7 No.	Yield %	m.p. °C	Formula (Mol. Wt)	Found/Calcd. %C	%H	%N
a	85	241-3	$C_{12}H_{12}N_4O_4Cl_2$ (347)	41.66 41.50	3.55 3.46	16.21 16.12
b	80	256-9	$C_{14}H_{16}N_4O_4Cl_2$ (375)	44.93 44.80	4.39 4.26	15.18 15.00
c	83	273-5	$C_{18}H_{24}N_4O_4Cl_2$ (431)	50.31 50.11	5.71 5.56	13.16 13.00
d	82	287-9	$C_{20}H_{28}N_4O_4Cl_2$ (459)	52.28 52.28	6.10 6.10	12.20 12.20

Preparation of bis phenoxyacetyl benzdioxazole 8_{a-d}

Substituted phenoxyacetyl chloride (2 mol) in dioxane 10 ml and triethylamine (2 mol) was refluxed with 1 (1 mol) for 2 hours. The reaction mixture was then allowed to stand at room temperature overnight. The precipitated triethylamine hydrochloride was filtered, the filtrate was evaporated under vacuum and the residue was

crystallized from ether and recrystallized from ethyl acetate.

Table 5 represents the physical and analytical data of 8.

TABLE 5

Comp. 8 No.	Yield %	m.p. °C	Formula (Mol. Wt)	Found/Calcd. %C	%H	%N
a	90	209-11	$C_{24}H_{14}N_4O_{10}$ (518)	55.48 55.60	2.59 2.70	10.70 10.81
b	91	196-8	$C_{24}H_{14}N_2O_4Cl_2$ (497)	57.81 57.94	2.69 2.81	5.51 5.62
c	89	215-7	$C_{24}H_{14}N_4O_{10}$ (518)	55.45 55.60	2.55 2.70	10.69 10.81
d	90	224-6	$C_{24}H_{14}N_2O_4Cl_2$ (497)	57.78 57.94	2.70 2.81	5.50 5.62

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Synthesis of 2,2′-Imino-Bis Thiazoles

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A number of 2, 2′-imino-bis thiazoles were prepared using Hantzsch thiazole synthesis by condensing 2-haloketone with thiazolyl thiourea.

BIS THIAZOLE unit has been found to occur in a number of antibiotics like micrococcin, saramycetin and bleomycin[1-6]. This unique system, which constitutes the backbone of these compounds is believed to play an important role in the biological activities of these natural products. It was, therefore, thought that the synthesis of such compounds would be an interesting problem in continuation with our study of potentially active sulphur compounds. This paper is, therefore, devoted to the preparation of 2,2′-imino-bis-4,4′-(substituted phenyl)-thiazoles.

All the title compounds described in this work, were synthesised by following Hantzsch thiazole synthesis, from the corresponding 2-haloketones and the thiazolyl thioureas. This method was preferred to dithiobiuret[7] method and Ullman type condensation[8], because of the absence of any six reactions and of good yields. Moreover, thiazolyl thioureas are important intermediates in that they are likely to possess activity[9].

Following 2-haloketones and substituted thioureas were used for the preparation of 2,2′-iminobis thiazoles.

(A) 2-Haloketones :

(1) 2, 4′-Dichloro acetophenone.
(2) 2, 3′, 4′-Trichloro acetophenone.
(3) 2, 2′, 5′-Trichloro acetophenone.
(4) 2, 2′-Dichloro-5′-methyl acetophenone.
(5) 2′-Bromo-5′-methyl-2-chloro acetophenone.
(6) Ethyl-α-chloro aceto acetate.

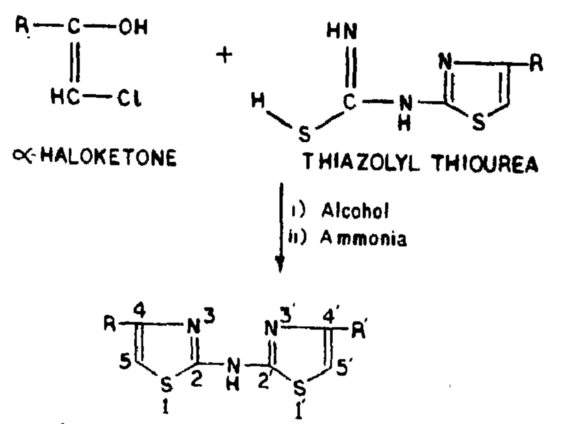
(B) Thiazolyl thioureas :

(1) 1-(2-(4-phenyl thiazolyl) thiourea.
(2) 1-(2-(4-*p*-chlorophenyl thiazolyl)) thiourea.
(3) 1-(2-(4-(2′-Hydroxy-5′-chlorophenyl)-thiazolyl)) thiourea.

2-Haloketones (1-5) were prepared from the corresponding hydrocarbons using Friedel and Craft's method, whereas ethyl-α-chloroaceto acetate was prepared by chlorinating active methylene group with sulphuryl chloride[10].

Thiazolyl thioureas were prepared from the 2-amino thiazoles by following Kurzer's method[11].

Condensation of 2-haloketone with thiourea in the presence of alcohol gave smoothly 2,2′-imino-bis thiazole hydrochloride, which upon basification with ammonium hydroxide solution yielded the free base (Fig. 1.). The formation of these compounds was confirmed from their elemental analysis (Table 1).



2,2′-Iminobis-4,4′-disubstituted thiazole

Fig.1.

TABLE 1- MELTING POINTS AND ELEMENTAL ANALYSIS OF 2, 2′-IMINOBIS THIAZOLES.

Compound No.	2, 2′-Iminobis thiazoles (only 4 and 4′-substituents are given).	M.P. °C	Molecular formula	Carbon % Required	Carbon % Found	Hydrogen % Required	Hydrogen % Found
1.	4-(2′-Chloro-5′ methyl phenyl)-4′-(p-chlorophenyl)-	202	$C_{19}H_{13}N_3Cl_2S_2$	54.54	55.68	3.11	3.55
2.	4-(phenyl)-4′-methyl-5′-carbethoxy-	210	$C_{16}H_{15}N_3O_2S_2$	55.65	55.64	4.34	4.44
3.	4-(4′-Chlorophenyl)-4′-methyl-5′-carbethoxy-	198	$C_{16}H_{14}N_3ClO_2S_2$	50.67	50.97	3.68	3.06
4.	4-(2′-bromo-5′-methyl phenyl)-4′(p-chlorophenyl)-	195	$C_{19}H_{13}N_3BrClS_2$	49.29	50.50	2.81	3.01
5.	4-(3′, 4′-Dichlorophenyl)-4′-phenyl-	145	$C_{18}H_{11}N_3Cl_2S_2$	53.47	54.08	2.72	3.41
6.	4-(3′, 4′-Dichlorophenyl)-4′-(p-chlorphenyl)-	155	$C_{18}H_{10}N_3Cl_3S_2$	49.26	49.90	2.28	2.55
7.	4-(2′, 5′-Dichlorophenyl)-4′-(p-chlorophenyl)-	200	$C_{18}H_{10}N_3Cl_3S_2$	49.26	50.08	2.28	3.12

Experimental

Preparation of 2,2'-iminobis thiazoles

A mixture of 2-haloketone (0.01 mole), substituted thiazolyl thiourea (0.01 mole) and alcohol (25 ml) was refluxed on a water bath for about two hours. The solid thus separated was filtered and washed with ether to remove unreacted ketone and thiourea. It was then boiled with water and ammonia solution whereby free base was obtained. It was filtered, washed with water and crystallised from acetone.

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Synthesis of 2-Sulfanilamido Thiazole Derivatives and Their Antibacterial Activity

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Some 2-amino-4-(disubstituted phenyl)-5-methyl thiazoles were synthesised and then converted to a number of sulfanilamido derivatives. The title compounds were tested for antibacterial activity.

THE thiazole analogues of sulfapyridine were earlier prepared and tested for chemotherapeutic activity[1,2]. Desai *et al*[3] reported the synthesis of a series of N-heterocyclic substituted sulfonamides and found that 4-amino-N-(4, 5-dimethyl-2-thiazolyl)-1-naphthalene sulfonamide was the most active of all other thiazole derivatives against *S. aureus* and *S. coli*. 4-Amino-N-(5-methyl-2-thiazolyl)- and 4-amino-4-(4, 5-dimethyl-2-thiazolyl)-benzene sulfonamides were also found to be active against bacterial infection[4]. We report herein the synthesis of some 2-amino-4-(2'-methoxy-3'/5' substituted phenyl)-5-methyl thiazoles and their sulfanilamido derivatives, with chloro and methyl substituents and their screening for antibacterial activities.

The *o*-methoxy propiophenones required as the starting material were obtained by the Fries migration of substituted propiophenones and methylation of the *o*-hydroxy propiophenones. The 2-amino thiazoles were prepared[5] by the condensation of substituted propiophenones with thiourea in presence of iodine. These 2-amino-4-(substituted phenyl)-5-methyl thiazoles (Table 1) were then treated with *p*-substituted benzene sulfonyl chlorides to get 2-sulfanilamido thiazole derivatives. The compounds containing acetamido group were hydrolysed to give the corresponding amino compounds.

The IR spectra of 2-amino-4-(substituted phenyl)-5-methyl thiazole showed absorption in the range of 3120 to 3480 cm^{-1} with higher intensity and at 1610 to 1645 cm^{-1} due to N-H stretching and bending vibrations respectively. The thiazole nucleus had characteristic absorption at around 1530, 1400, 1380, 1020, 800 cm^{-1}. The respective asymmetric and symmetric stretching modes of vibration of S=O from sulfanilamido group appeared in the range of 1380 to 1335 and 1170 to 1160 cm^{-1}.

Experimental

Synthesis of 2-amino-4-(substituted phenyl)-5-methyl thiazoles (I): A mixture of substituted propiophenone (0.1 mol), thiourea (0.25 mol, 19 g) and iodine (0.1 mol, 25.4 g) was heated on water-bath for 26 hr. The 2-amino-4-(substituted phenyl)-5-methyl thiazole was isolated following the method

TABLE 1. 2-AMINO-4-(SUBSTITUTED PHENYL)-5-METHYL THIAZOLES

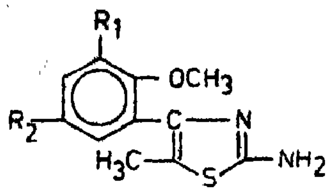
Compd. no.	M.p. °C	Yield %	Mol. formula	Elemental analysis: Found C%	H%	Requires C%	H%
Ia	204	64	$C_{11}H_{11}ON_2SCl$	51.54	4.00	51.96	4.33
Ib	146	75	$C_{11}H_{11}ON_2SCl$	51.61	4.21	51.96	4.33
Ic	194	71	$C_{12}H_{14}ON_2S$	61.05	5.51	61.58	5.98

TABLE 2. 2-SULFANILAMIDO-4-(SUBSTITUTED PHENYL)-5-METHYL THIAZOLES

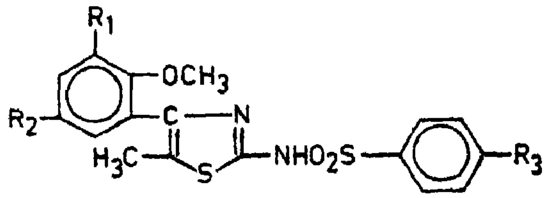
Compd. no.	M.p. °C	Yield %	Mol. formula	% S Found	Requires
IIa	130	85	$C_{17}H_{17}O_3N_3S_2Cl$	15.21	15.68
IIb	169	85	$C_{17}H_{17}O_3N_3S_2Cl$	15.32	15.68
IIc	188-9	64	$C_{18}H_{20}O_3N_3S_2$	16.51	16.49
IId	257	59	$C_{17}H_{14}O_3N_3S_2ClBr$	13.00	13.14
IIe	171	57	$C_{17}H_{14}O_3N_3S_2ClBr$	13.20	13.24
IIf	145	59	$C_{17}H_{14}O_3N_3S_2Cl$	16.10	15.80
IIg	105	69	$C_{19}H_{18}O_4N_3S_2Cl$	13.92	14.19
IIh	162	77	$C_{19}H_{18}O_4N_3S_2Cl$	13.89	14.19
IIi	338	78	$C_{20}H_{21}O_4N_3S_2$	14.60	14.84
IIj	84	68	$C_{17}H_{16}O_3N_3S_2Cl$	15.51	15.69
IIk	150	78	$C_{17}H_{16}O_3N_3S_2Cl$	15.15	15.69
IIl	298	79	$C_{18}H_{19}O_3N_3S_2$	16.10	16.45

* For correspondence.

of Dodson and King[5] and crystallised from ethanol. The data are given in Table 1.



I



II

I a R_1=Cl, R_2=H.
b R_1=H, R_2=Cl.
c R_1=H, R_2=CH_3.

II a R_1=Cl, R_2=H, R_3=CH_3.
b R_1=H, R_2=Cl, R_3=CH_3.
c R_1=H, R_2=CH_3, R_3=CH_3.
d R_1=Cl, R_2=H, R_3=Br.
e R_1=H, R_2=Cl, R_3=Br.
f R_1=H, R_2=CH_3, R_3=Cl.
g R_1=Cl, R_2=H, R_3=$NHCOOCH_3$.
h R_1=H, R_2=Cl, R_3=$NHCOOCH_3$.
i R_1=H, R_2=CH_3, R_3=$NHCOOCH_3$.
j R_1=Cl, R_2=H, R_3=NH_2.
k R_1=H, R_2=Cl, R_3=NH_2.
l R_1=H, R_2=CH_3, R_3=NH_2.

General procedure for the synthesis of 2-sulfanilamido-4-(substituted-phenyl)-5-methyl thiazoles (II) : A mixture of 2-amino-4-(substituted phenyl)-5-methyl thiazole (0.1 mol), *p*-substituted benzene sulfonyl chloride (0.11 mol) and dry pyridine (20 ml) was heated on water-bath for one hr and kept at room temp. for 48 hr. The reaction mixture was poured on to ice containing a little conc. H_2SO_4 with stirring. The crude product obtained was washed with dil. $NaHCO_3$ solution and finally with distilled water. It was crystallised from aq. ethanol. Methyl-, bromo-, chloro-, and acetamido- benzene sulfonyl chlorides were condensed with different 2-amino thiazoles to give 2-sulfanilamido-4-(substituted phenyl)-5-methyl thiazoles. The 2-(4'-acetamido sulfanilamido)-4-(substituted phenyl)-5-methyl thiazole derivatives were hydrolysed by 30% alc.HCl to 2-sulfanilamido-4-(substituted phenyl)-5-methyl thiazoles which were also crystallised from aq. ethanol. The data are given in Table 2.

Activity

All the 2-sulfanilamido thiazoles were tested against four different organisms, *viz. V. comma, M. tuberculosis, S. aureus* and *S. typhi.* In general, the compounds are active against *M. tuberculosis.* 2-Sulfanilamido-4-(2'-methoxy-3'-chlorophenyl)-5-methyl thiazole (IIj) was found to be the most active and its activity is quite comparable to that of streptomycin (H_{37} Rv/strain).

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Heterocyclic System : I. Reaction of 4-Oxo-4*H*-[I]-benzopyran-3-carboxaldehydes with Phenylhydrazine and Formation of 1-Phenyl-4-(2-hydroxybenzoyl)pyrazoles

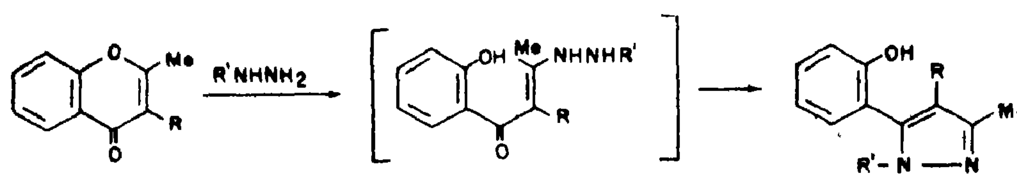
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Phenylhydrazine undergoes 1 : 2 addition to the aldehydic function of 4-oxo-4*H*-[1]-benzopyran-3-carboxaldehydes (I), the addition products on elimination of water giving the hydrazones (II). The latter on being refluxed in ethanolic potassium hydroxide yield 1-phenyl-4-(2-hydroxybenzoyl) pyrazoles (III). The mechanism of this transformation and the mass spectral fragmentation of the pyrazoles (III) have been discussed.

CHROMONES in their reactions with hydrazine or phenylhydrazine behave like α-β unsaturated ketones ; the nucleophile attacks at C-2 (Michael addition) with concomitant opening of the pyrone ring. The intermediate thus formed undergoes further conversion to 3(5)-*o*-hydroxyphenylpyrazole system[1,2].



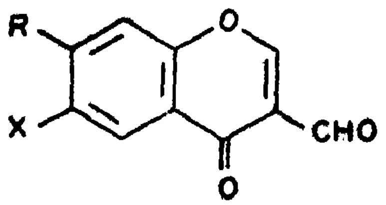
R = H or alkyl ; R' = H or Ph

It was our interest to investigate how 4-oxo-4*H*-[1]-benzopyran-3-carboxaldehydes (3-formylchromones) would behave towards phenylhydrazine. The present paper deals with the results of this investigation.

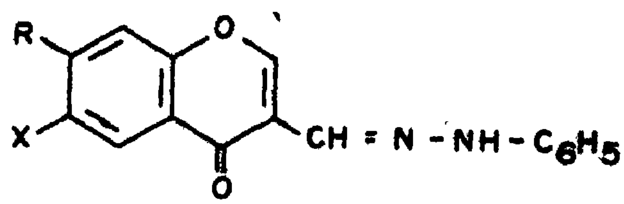
3-Formylchromones can be prepared either by formylating 2'-formyl-2-hydroxyacetophenones with ethyl orthoformate and acetic anhydride[3] or by the application of Vilsmeier Haack reaction to various *o*-hydroxyacetophenones as prescribed by Nohara *et al.*[4]. During the present course of investigation, however, the second method[4] was found to be most suitable.

3-Formylchromone (Ia) with phenylhydrazine gave at first a compound having m. p. 213 which did not give any colouration with ferric chloride. Its UV (ethanol) : 210 nm (log ε 4.16), 294 (4.16) and 345 (4.18) suggests that it has the same ring structural feature as that of the starting chromone-3-aldehyde (Ia) having UV (ethanol) : 213 (4.33), 305 (3.95) and 345 (3.96). The phenylhydrazone derivative has thus been assigned by structure (IIa). In this connection it may be noted that hydroxylamine hydrochloride as well as cyanoacetamide in presence of pyridine first attacks the aldehydic carbon of 3-formylchromones[5,6]. The hydrazone (IIa) on being refluxed with alcoholic potassium hydroxide afforded in quantitative yield 1-phenyl-4-(2-hydroxybenzoyl)pyrazole (IIIa), m. p. 113°, UV (ethanol) : 211 nm(log ε 4.48) and 289 (4.22) ; UV (ethanol, NaOH) ; 210 (3.42) and 270 (3.97) ; IR (nujol, cm^{-1}) : 3025 (very weak, chelated OH)[7], 1570 (s, aryl pyrazolyl ketone chelated with *ortho*-OH) ; NMR ($CDCl_3$, TMS)τ : −2.87 (br. 1H, ArOH)[6], 1.52 (s, 1H, pyrazole H_3), 1.82 (s, 1H, pyrazole H_5) and 2.05 − 3.20 (m, 9H, ArH) ; mass spectrum : 264 (M^+, base peak), 172, 171, 144, 121, 120, 93 and 92. The structure (IIIa) was also confirmed by the following experiments. It gave violet colouration with ferric chloride. It formed an acetate, IR (nujol) cm^{-1} : 1750 (s, ester carbonyl), 1625 (s, aryl pyrazolyl ketone), 1250 (O-acyl) ; NMR ($CDCl_3$, TMS)τ : 1.68 (s, 1H, pyrazole H_3), 1.93 (s, 1H, pyrazole H_5), 2.20 − 2.87(m, 9H, ArH) and 7.85 (s, 3H, $-COCH_3$). On oxidation with either chromic acid in acetic acid − acetone − water at room temperature, or alkaline potassium permanganate at reflux temperature it afforded 1-phenylpyrazole-4-carboxylic acid[8].

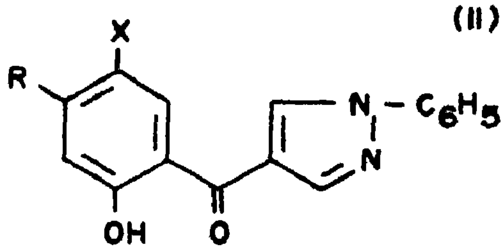
The formation of the pyrazole (IIIa) can be rationalised as follows : the hydroxide anion cleaves the pyrone ring of the chromone (IIa) at C-2 with the generation of an aldehyde function[9] that further reacts with the phenylhydrazino group present in the molecule (Scheme I). Various substituted 1-phenyl-4-(2-hydroxybenzoyl)pyrazoles (III) that were similarly prepared are listed in Table 1.



(I)



(II)



(III)

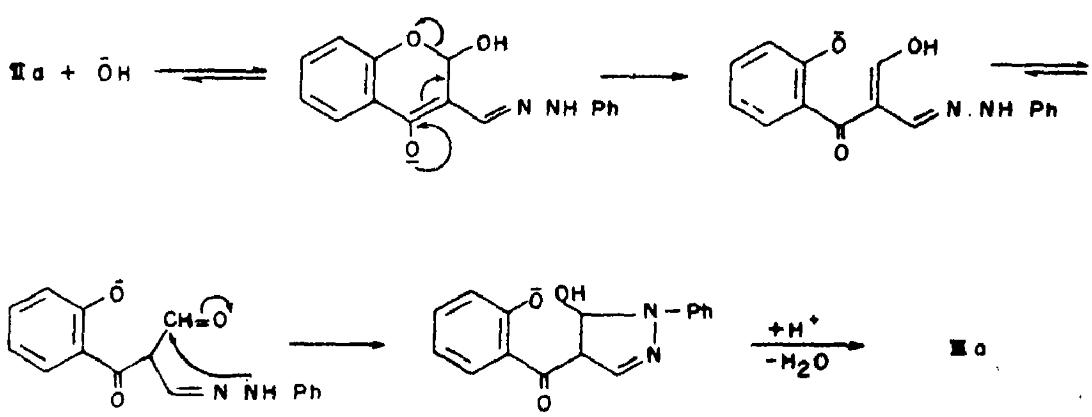
TABLE 1—Melting points (in °C) of 3-formylchromones (I), their phenylhydrazones (II), 1-phenyl-4-(2-hydroxybenzoyl)-pyrazoles (III) and the acetates of compounds (III).

Sl. No	Substituents R	Substituents X	Compound* (I)	Compound† (II)	Compound§ (III)	Acetate of (III)
a	H	H	154	213	113·	113
b	Me	H	170-72	—	114	114
c	H	Cl	163-65	172	145	97
d	H	Br	180	—	154	132
e	H	Me	171	210	121	—
f	H	OMe	158	207	121	—
g	Me	NO_2	140--43	270	252	—
h	H	NO_2	163	—	206-210	150

* Solvent of crystallisation : ethanol. Melting points of compounds (I) were very close to lit.[4b] m.p.s.

† Some of these compounds were not purified by crystallisation, hence their m.p.s are not recorded. Ethanol was used as solvent for crystallisation.

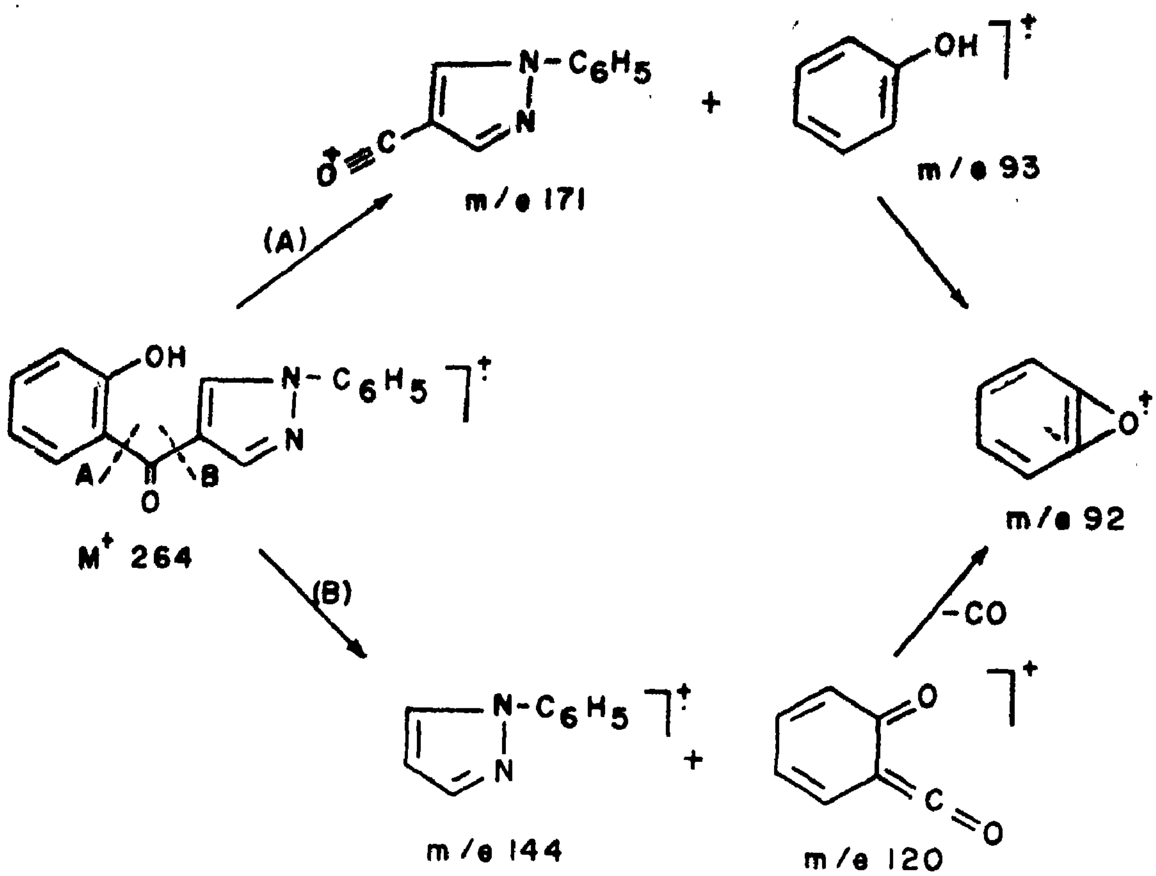
§ Solvent of crystallisation was either chloroform or chloroform-pet. ether ; yield 65-80% based on comp. (I).



Scheme - I

The fragmentation patterns of 1-phenyl-4-(2-hydroxybenzoyl) pyrazoles (III) in their mass spectra are exemplified in Scheme 2 for the parent compound (IIIa).

The highly aromatic character of the compound is shown by the great intensity of the molecular ion (base peak). By electron impact, the α-carbonyl bonds are susceptible to cleavage. Thus the molecular ion can undergo fragmentation in two different ways. α-Carbonyl cleavage (A) gives two fragments of m/e 171 and 93. By a concomitant hydrogen shift two fragments of mass units 172 and 92 are also obtained. The alternate α-carbonyl cleavage with subsequent hydrogen shift (B) produces two other fragments having m/e 144 and 120. A highly intense peak at m/e 121 is also obtained by a hydrogen shift to m/e 120 from any other ion. The m/e 144 ion may also be generated by loss of CO from the ion of m/e 172. The m/e 120 ion by elimination of CO collapses also to the ion of m/e 92.



Scheme—2

Experimental

Formylchromones (Ia – f) were prepared from properly substituted 2-hydroxyacetophenones[4]. The experimental procedure for the preparation of 3-formylchromone (Ia) is described here as a representative case.

3-Formylchromone (Ia). N,N-dimethylformamide (45 ml) was cooled in ice-salt mixture and stirred magnetically. Phosphorus oxychloride (20 ml, 0.22 mole) was slowly added to it. Pink colour of the formylating complex appeared. *o*-Hydroxyacetophenone (13.6 g, 0.10 mole) was added drop by drop. Some time after the addition was over, the reaction mixture set to a thick mass, and it was left overnight at room temp. Next day, the semi-solid mass was decomposed by addition of water. The precipitated solid was filtered and recrystallised from ethanol to afford 3-*formylchromone* (Ia) (9.0 g), m.p. 154°, yield 52%.

Nitrochromones (Ig-h). These were prepared by nitrating the chromones (Ia) and (Ib) respectively[4b]. In a typical procedure, the proper chromone (0.02 mole) was added pinch by pinch to a cooled and stirred mixture of conc. sulphuric acid (10 ml) and conc. nitric acid (10 ml). The reaction mixture was left at room temp. for 1 hr, warmed for 10 min on a water bath, and then poured in ice-water. The solid deposited was filtered, washed with water, and recrystallised from ethanol.

Phenylhydrazones (II) of 3-formylchromones (I). A warm solution of phenylhydrazine hydrochloride (0.72 g, 0.005 mole) and sodium acetate (1.40 g) in water (2-3 ml) was added at a time to formylchromone (I) (0.005 mole) dissolved in ethanol (2-3 ml) when yellow coloured hydrazone (II) separated out. The yield of the compound (II) was over 90% in each case.

1-Phenyl-4-(2-hydroxybenzoyl)pyrazole (IIIa). The hydrazone (IIa) (0.50 g) was refluxed with a solution of potassium hydroxide (1.0 g) in water (2 ml) and ethanol (10 ml) for 1 hr. After cooling, the solution was diluted with water and acidified with acetic acid. The solid deposited was filtered and recrystallised from chloroform in light yellow crystals of the *pyrazole* (IIIa) (0.41 g), m.p. 113°. On refluxing with acetic anhydride and pyridine, it furnished an *acetate*, m.p. 113° (CH_3COOH).

All other hydrazones (II) were similarly converted to the pyrazoles (III).

Oxidation of 1-phenyl-4-(2-hydroxybenzoyl) pyrazole (IIIa). (a) *With chromium trioxide* :—A mixture of the compound (IIIa) (0.50 g), acetone (5 ml), acetic acid (3 ml), water (1 ml) and chromium tri-

oxide (1.0 g) were stirred magnetically at room temperature for 4 hr. It was then diluted with water and organic matter extracted with chloroform. The chloroform extract on concentration yielded *1-phenylpyrazole-4-carboxylic acid* (0.30 g), m.p. 221° (ethyl acetate – pet. ether) (lit.[8], m.p. 219-20°). On treatment with diazomethane it gave the corresponding *methyl ester*, m.p. 127° (ethyl acetate – pet. ether) (lit.[8], m.p. 128-9°).

(b) *With potassium permanganate* :—A mixture of the pyrazole (IIIa) (1.0 g), potassium permanganate (2 g), sodium hydroxide (3 g) and water (15 ml) was refluxed for 3 hr, then cooled and filtered. The filtrate on acidification yielded *1-phenylpyrazole-4-carboxylic acid* (0.3 g), m.p. 221° (alcohol-water). When admixed with the chromic acid oxidation product of the pyrazole (IIIa), it melted at 221°.

Acknowledgement

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Kinetics of Ce(IV) Oxidation of Diethyl Ketone in Sulphuric Acid Solutions

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The kinetic data on Ce(IV) oxidation of diethyl ketone in sulphuric acid solutions at four temperatures show first order dependence of the reaction on both Ce(IV) and diethyl ketone. The reaction rate decreases on increasing the ionic strength of the medium while it increases on increasing the concentration of hydrogen ions. The reaction rate is unaffected by the change in concentration of both sulphate and bisulphate ions.

FEW ketones have already been subjected to kinetic studies with interest because of their various possible species involved in reactions. Earlier workers[1-6] have reported kinetic data on oxidation of ketones by different oxidants including Ce(IV) in various media. Shorter[6] has made comparative survey of the reactivities and stoichiometry for acetaldehyde and a series of ketones including diethyl ketone at 70°, but he has not made detailed study of kinetics and mechanism of Ce(IV) oxidation of diethyl ketone. In the present communication an attempt has been made to obtain the kinetic data for the reaction between Ce(IV) and diethyl ketone in the temperature range 35°-50°.

Experimental

Materials and Method : Diethyl ketone (Fluka) grade and ceric sulphate (E. Merck) G.R. quality were used as such without further purification. Other chemicals e.g. ferrous ammonium sulphate, sulphuric acid and potassium sulphate were of A. R. (B. D. H.) grade and samples of sodium hydrogen sulphate and ferroin were of (Sarabhai, M) and (E. Merck) respectively but samples of perchloric acid and sodium perchlorate were of (Riedel) grade.

A stock solution of ceric sulphate was prepared by direct weighing in $5N$ H_2SO_4 and was standardised against ferrous ammonium sulphate using ferroin as redox indicator.

The reaction was initiated by adding a temperature equilibrated solution of diethyl ketone to a reaction vessel (maintained at desired temperature) containing the required amounts of sulphuric acid, ceric sulphate solution and water. The kinetics were followed by removing 5 ml aliquots after different intervals of time and quenching the reaction by known excess of ferrous ammonium sulphate solution. The excess of ferrous ammonium sulphate was estimated by standard ceric sulphate solution using ferroin as redox indicator.

Results and Discussion

Stoichiometry : The equivalents of Ce(IV) used per mole of ketone was found to be 14 at 40° in $2N$ sulphuric acid and reaction products identified by TLC are propionic and acetic acids. These results suggest that before triketone is formed as assumed by shorter[6], diketone probably undergoes fission and thus other methylene group escapes the attack.

Dependence of Reaction on Reactants : About sixfold variation in Ce(IV) concentration (Table 1) showed that order in Ce(IV) is one. Straight lines were obtained by plotting log $[Ce(IV)]_t$ versus time and the pseudo-first order constants were calculated from the slopes of these lines (Fig 1).

TABLE—1

Temperature 40° ; [Diethyl-ketone] = 4.00×10^{-3} ; M [H_2SO_4] = 2.00N

[Ceric sulphate] $\times 10^3$ N	5.00	4.00	2.50	2.00	1.66	1.34
$k_1 \times 10^3$ min^{-1}	12.08	12.06	13.24	12.28	12.67	12.15

Average value of $k_1 = 12.41 \times 10^{-3}$ min^{-1}

About sixfold variation in diethyl ketone concentration (Table 2) showed that pseudo-first order rate constants in Ce(IV) were directly proportional to diethyl ketone concentrations. The constancy of k_2 values (second order rate constants) shown in last column of Table 2 clearly indicates that reaction follows first order kinetics in diethyl ketone also.

TABLE—2

Temperature 40° ; [Ceric sulphate] = 2.00×10^{-3}N ; [H_2SO_4] = 2.00N

[Diethyl ketone] $\times 10^2$ M	10.00	6.66	5.00	4.00	2.50	1.66
$k_1 \times 10^3$ min^{-1}	32.49	20.70	15.11	12.37	7.95	5.08
$k_2 \times 10$ l. mole^{-1} min^{-1}	3.25	3.11	3.02	3.09	3.18	3.05

Average value of $k_2 = 3.10 \pm 10^{-1}$ l. mole^{-1} min^{-1}

* To whom correspondence should be made.

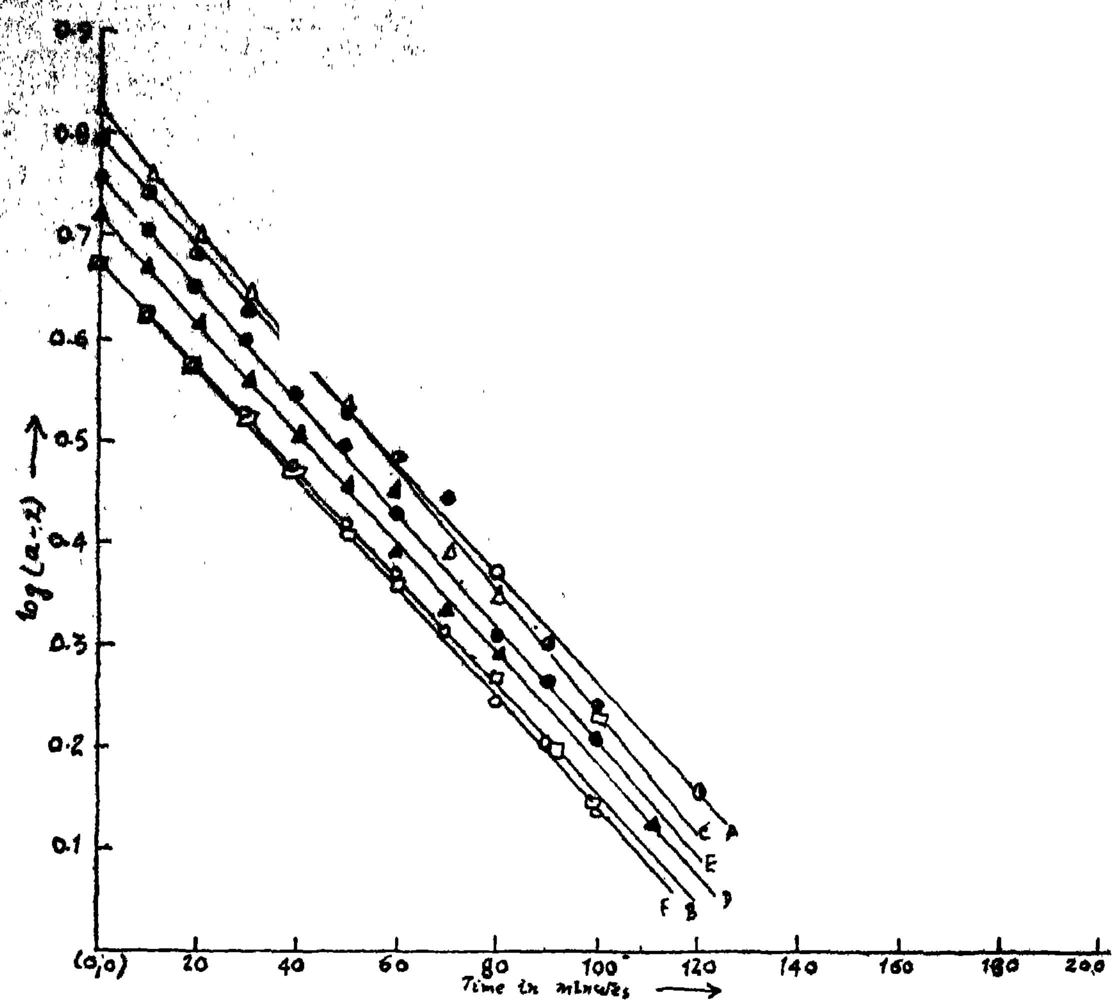


Fig. 1.

Temperature 40°
[Diethyl ketone]$=4.00\times10^{-2}M$
[Sulphuric Acid]$=2.00N$

[Ceric sulphate] 10^{4}N: A=5.00, B=4.00, C=2.50, D=2.00, E=1.66, F=1.33

Plot	$10^{4}\times K_1$ min^{-1} (from the slope)
A	12.09
B	12.06
C	13.24
D	12.28
E	12.67
F	12.15

Effect of Ionic Strength, Sulphate, Bisulphate and Hydrogen Ions

The reaction velocity decreased to the extent of 25% on increasing the ionic strength of the medium by six times. This substantial change in rate could not be explained specially when ionic strength variation falls beyond Debye-Hückel limiting law. About tenfold variation in the concentrations of both sulphate and bisulphate ions did not produce any perceptible change in rate (Table 3), which is different from usual observations made by earlier workers[7-18]. The reaction velocity increased more than two times on increasing the concentration of sulphuric acid from 1.5 to 6.0 N. This increase is definitely due to hydrogen ions as sulphate and bisulphate ions do not affect the rate. This observation was, further, confirmed by variation of perchloric acid[19-20] at fixed concentration of sulphuric acid and constant ionic strength. A ten-

fold variation in perchloric acid concentration enhanced the velocity by about twofold. A graph between Δk_1 (difference between rate constants of the reaction with perchloric acid and without perchloric acid) and $\Delta[H^+]$ (difference of hydrogen ions in presence of perchloric acid and in absence of perchloric acid) was plotted. A straight line passing through origin clearly indicates the positive effect of hydrogen ions.

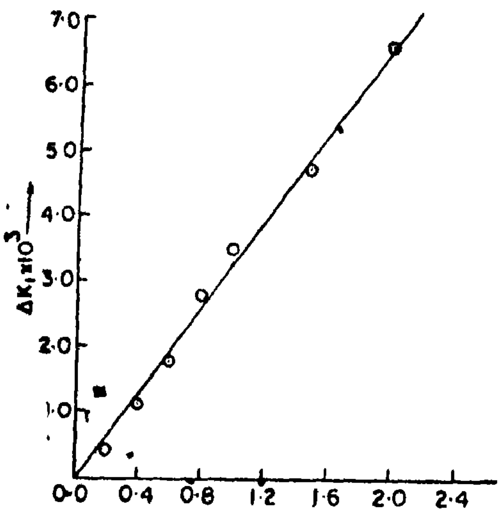


Fig. 2

Temperature 40°
[Diethyl Ketone] = 4.00×10^{-2} M
[Ceric sulphate] = 2.00×10^{-3} N
[Sulphuric acid] = 2.00 N
μ = 3.024 M

Kinetic data on temperature effect were given in Table 3. The values of energy of activation (ΔE), entropy of activation (ΔS^*), free energy (ΔF^*) and frequency factor (A) are 18.5 K. cals/mole, −1.2 E.U., 22.3 K. cals/mole and 33.1×10^9 l. mole^{-1} sec^{-1} respectively.

Ketones provide three possible real sites of attack viz. either negative, neutral or positive forms. The positive form is ruled out on the basis of transfer of electrons from ketone to ceric species in ceric sulphate oxidation of ketones. Our kinetic results do not allow us to assume the negative ion to be active form of ketone (the condition for which is that hydrogen ion concentration[4] should lower the rate). Therefore, enol (neutral) form of ketone is only obvious choice for the real site of attack. Earlier workers[4,21,22] also support this postulate.

Cerium(IV) has been reported to exist in many species by earlier workers[23,24]. $[Ce(SO_4)]^{2+}$, $Ce(SO_4)_2$ and $[Ce(SO_4)_3]^{2-}$ species of Ce(IV) have been shown in equilibria by Hardwick and Robertson[19] in sulphuric acid solution. Hargreaves and Sutcliffe[25] have also suggested some equilibria involving $[HCe(SO_4)_4]^{3-}$, $[H_2Ce(SO_4)_4]^{2-}$, $[H_3Ce(SO_4)_4]^-$ and $H_4Ce(SO_4)_4$ ions to explain mechanism of certain reactions. Our observations lead us to assume that $[HCe(SO_4)_3]^-$ is the reactive species. Absorption spectra studies of Bugaenko and Hwang Kuan-Lin (*Russ. J. Inorg. Chem.* (*1963*)) **8**, 1299 also support this. The proposed reactive species (1) i.e. $[H\,Ce(SO_4)_3]^-$ is supposed to be in equilibrium with another species (2) as given below.

$$[H\,Ce(SO_4)_3]^- \text{ species(1)} + H^+ \overset{K_1}{\rightleftharpoons} \text{species (2)} \; [H_2Ce(SO_4)]_3 \ldots\ldots (i)$$

TABLE—3

[Ceric sulphate] = 2.00×10^{-3} N. [Diethyl ketone] = 4.00^{-2} M; μ = 3.024 M

Temp. in °C	$[H_2SO_4]$ N	$[HClO_4]$ N	$[K_2SO_4]$ N[a]	$[NaHSO_4]$ N	$k_1 \times 10^3$ min^{-1}
40	1.5	—	—	—	4.37
,,	2.0	—	—	—	4.97
,,	3.0	—	—	—	6.13
,,	4.0	—	—	—	7.42
,,	5.0	—	—	—	8.58
,,	6.0	—	—	—	10.99
40	2.0	0.20	—	—	5.35
,,	,,	0.40	—	—	5.60
,,	,,	0.60	—	—	6.79
,,	,,	0.80	—	—	7.78
,,	,,	1.00	—	—	8.51
,,	,,	1.50	—	—	9.69
,,	,,	2.00	—	—	11.49
40	2.0	—	0.01	—	10.76
,,	,,	—	0.02	—	11.05
,,	,,	—	0.01	—	10.84
,,	,,	—	0.08	—	10.12
,,	,,	—	0.10	—	10.20
40	2.0	—	—	0.2	4.86
,,	,,	—	—	0.4	4.72
,,	,,	—	—	0.8	4.84
,,	,,	—	—	1.2	4.85
,,	,,	—	—	1.6	4.83
,,	,,	—	—	2.0	4.97
35 b	2.0	—	—	—	6.25
45 b	,,	—	—	—	15.09
50 b	,,	—	—	—	25.10

a → μ = 1.774 M; b → μ = 1.024 M

species (2) forms a complex with the enol form of ketone. Finally the complex undergoes redox reaction.

The complete mechanism for Ce(IV) oxidation of diethyl ketone in sulphuric acid solutions may, thus, be proposed as noted below

$$C_2H_5.CO.C_2H_5 + H^+ \overset{K_2}{\rightleftharpoons} C_2H_5.C\langle^{(OH)}_{CH.CH_3} \quad ......(ii)$$

$$C_2H_5.C\langle^{(OH)}_{CH.CH_3} + \underset{(species\ 2)}{H_2Ce(SO_4)_3} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Complex(C) \quad ......(iii)$$

$$C \xrightarrow{k'_3} Ce(III) + Reaction\ products \quad .....(iv)$$

Now by applying stationary state treatment to the concentration of complex, the above scheme leads to the following rate expression

$$\frac{-d[Ce(IV)]}{dt} = \frac{K_1K_2k'_3k_3}{k_{-3}} [Ceric]\ [diethyl\ ketone]\ [H^+] \quad ......(v)$$

$$or\ rate = k_4[Ce(IV)]\ [diethyl\ ketone]\ [H^+] \quad ......(vi)$$

where $k_4 = K_1K_2k'_3k_3/k_{-3}$

Thus the rate expression (vi) fully explains our kinetic data which are not explained by any other reaction path.

When the reaction is studied at fixed concentration of hydrogen ions, the equation (vi) becomes

$$\frac{-d[Ce(IV)]}{dt} = k_2\ [diethyl\ ketone]\ [Ce(IV)] \quad .....(vii)$$

and when [diethyl ketone] $\gg$ [Ce(IV)], we have

$$\frac{-d[Ce(IV)]}{dt} = k_1\ [Ce(IV)] \quad ....(viii)$$

Equation (viii) shows that the reaction follows first order kinetics in Ce(IV) which shows the validity of our proposed mechanism.

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Solvent Effect on Amide Hydrolysis. III—Kinetics of Formamide Hydrolysis in isoPropanol-Water Mixtures

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Solvent effects on the acid and base hydrolysis of formamide were investigated in isopropanol-water mixtures, up to 75.06 wt % of the alcohol, at the temperature range 25-60°. *Both reactions are retarded by increasing the concentration of isopropanol,* but in case of the base hydrolysis the rate increases on further progressive addition of the alcohol passing through a minimum at about 34 wt % of isopropanol. Temperature, *dielectric constant, solvent composition,* activation parameters, acidity function and medium effects on reaction rates and mechanisms are briefly discussed.

THE kinetics and mechanisms of formamide hydrolysis were recently studied in this laboratory, in acidic and basic dioxane- and n.propanol-water mixtures[1]. The results were analysed and discussed in the light of our proposed mechanisms of the acid and base hydrolysis. In the present work we have studied the solvent effects on the kinetics and mechanism of formamide hydrolysis in isopropanol-water solutions of different compositions. This was undertaken to decide also the validity of our previously proposed correlations of reaction rate[1].

Experimental

Materials and Kinetic Procedure

The purification of formamide or isopropanol was described before[2]. AnalaR or B D H materials were generally used. Boiled deionised water was used throughout all the experimental work. The rate of the acid or base hydrolysis of formamide in isopropanol-water mixtures, up to 75.06% by weight of the alcohol, was determined by the same procedure mentioned in our previous work[3,4]. The initial concentrations of both amide and acid or base were always constant and equal to 0.1*M*. The temperature was held constant within ±0.05°. Measurements were repeated at least two times and all rate constants listed are the mean of at least three completely independent determinations.

Results and Discussion

Temperature Effect on Reaction Rate

The effect of temperature on the rate of acid or base hydrolysis of formamide was investigated in five isopropanol-water mixtures (7.95, 16.25, 34.08, 64.32 and 75.06 wt % of isopropanol). Rate constants in liter mole^{-1} second^{-1} were measured at five different temperatures (25, 35, 40, 50 and 60°). The results are collected in Table 1. Both re-

TABLE 1—KINETIC RESULTS OF FORMAMIDE HYDROLYSIS IN ISO-PROPANOL-WATER MIXTURES

Iso-Propanol wt %		7.95	16.25	34.08	53.49	64.32	75.06
log $C_{solvent}$		0.115	0.417	0.718	0.894	0.961	1.015
log C_{water}		1.701	1.639	1.517	1.342	1.232	1.051
				I—*Acid Hydrolysis*			
25°	D	72.79	66.80	53.91	39.88	32.42	26.16
	22+L	3.900	3.696	3.203	2.699	2.305	1.641
	5+log k_2	1.246	1.146	1.053	0.989	0.932	0.901
35°	D	69.36	63.54	51.28	37.77	30.58	24.55
	5+log k_2	1.621	1.520	1.475	1.382	1.339	1.310
40°	D	67.62	62 01	49.94	36.78	29.79	23.93
	5+log k_2	1.803	1.707	1.665	1.589	1.534	1.516
50°	D	64.59	59.12	47.41	34.78	28.14	22.52
	5+log k_2	2.155	2.065	2.013	1.959	1.922	1.901
60°	D	61.82	55.66	44.19	32.44	26.68	21.24
	5+log k_2	2.485	2.401	2.362	2.319	2.279	2.258
E_c		16.06	16.48	16.92	17.28	17.53	17.76
log A		8.02	8.17	8.45	8.64	8.78	8.91
				II—*Base Hydrolysis*			
25°	D	72.79	66.80	53.91	39.88	32.42	26.16
	22+L	5.005	4.716	4.325	3.652	3.357	2.449
	5+log k_2	2 269	2.206	2.145	2.160	2.177	2.229
35°	D	69.36	63.54	51.28	37.77	30.58	24.55
	5+log k_2	2.606	2.523	2.461	2.476	2.498	2.545
40°	D	67.62	62.01	49.94	36.78	29.79	23.93
	5+log k_2	2.764	2.672	2.611	2.623	2.641	2.699
50°	D	64.59	59.12	47.41	34.78	28.14	22.52
	5+log k_2	3.066	2.961	2.892	2.903	2.928	2.989
60°	D	61.82	55.66	44.19	32.44	26.68	21.24
	5+log k_2	3.345	3.238	3.162	3.183	3.201	3.266
E_e		14.03	13.66	13.58	13.51	13.44	13.35
log A		8.15	7.12	7.09	7.06	7.04	7.01

actions are inhibited by increasing the concentration of the organic component, but in case of the base hydrolysis the rate increases on further progressive addition of isopropanol passing through a minimum at about 34 wt % of isopropanol. The isocomposition (E_c) and isodielectric (E_d) activation energies were calculated (Tables 1 and 2) from the very good followed Arrhenius plots in this wide range of temperatures. It can be seen that both activation energies increase with successive addition of isopropanol in the acid hydrolysis, *whereas they decrease in the base hydrolysis*. This may reflect the dependence of the reaction rate on the solvent composition.

Table 2—Refined $a_{\neq}$ Values (in A) and Isodielectric Energies of Activation (in kcal/mole) at Chosen D Values.

Dielectric Constant		10	20	40	60	80
		I—Acid Hydrolysis				
$a_{\neq}$ at	25°	7.3	7.7	8.0	8.2	8.5
	35°	7.3	7.7	8.0	8.2	8.5
	40°	7.3	7.7	8.0	8.2	8.5
	50°	7.4	7.8	8.1	8.3	8.6
	60°	7.4	7.8	8.1	8.3	8.6
E_d		18.88	18.53	17.84	17.07	16.75
		II—Base Hydrolysis				
$a^{\neq}$ at	25°	6.2	6.4	6.6	6.7	6.8
	35°	6.2	6.4	6.6	6.7	6.8
	40°	6.2	6.4	6.6	6.7	6.8
	50°	6.3	6.5	6.7	6.8	6.9
	60°	6.3	6.5	6.7	6.8	6.9
E_d		14.19	13.85	13.81	14.67	15.43

Dielectric Constant Effect on Reaction Rate

Both the Laidler-Landskroener equation of ion-neutral molecule interaction[4] and Amis equation of ion-dipole interaction[6] involve a linear correlation of the logarithm of the velocity constant ($\log k_2$) with reciprocal of the dielectric constant (1/D) in aqueous-organic solvents. However, the plots of $\log k_2$ versus 1/D for the various isopropanol-water compositions reveal that the rate decreases first linearly with decrease of the dielectric constant, then a curvature occurs specially at low dielectric constants. This behaviour, generally found with electrostatically influenced rates, is due to selective solvation by the higher dielectric constant component (water) of the *mixed solvent*[7]. The dielectric constant values of isopropanol-water mixtures were obtained by interpolation from sufficiently large-scale plots of Åkerlöf's data[8].

The effect of dielectric constant on rate of hydrolysis of formamide in isopropanol-water mixtures can best be described by the Elsemongy's equation[7].

$$k = k' \ e^{a(D-1)} \ ,$$

where k is the rate constant, k' is the rate constant under the conditions of the standard state (D = 1), and a is a constant. This equation predicts a linear dependence of $\log k_2$ on D at any temperature. Fig. 1 shows that the plots of $\log k_2$ versus D gave very good straight lines. The rate constants, k', for the acid (k'_a) and base (k'_b) hydrolysis of formamide in isopropanol-water mixtures were deter-

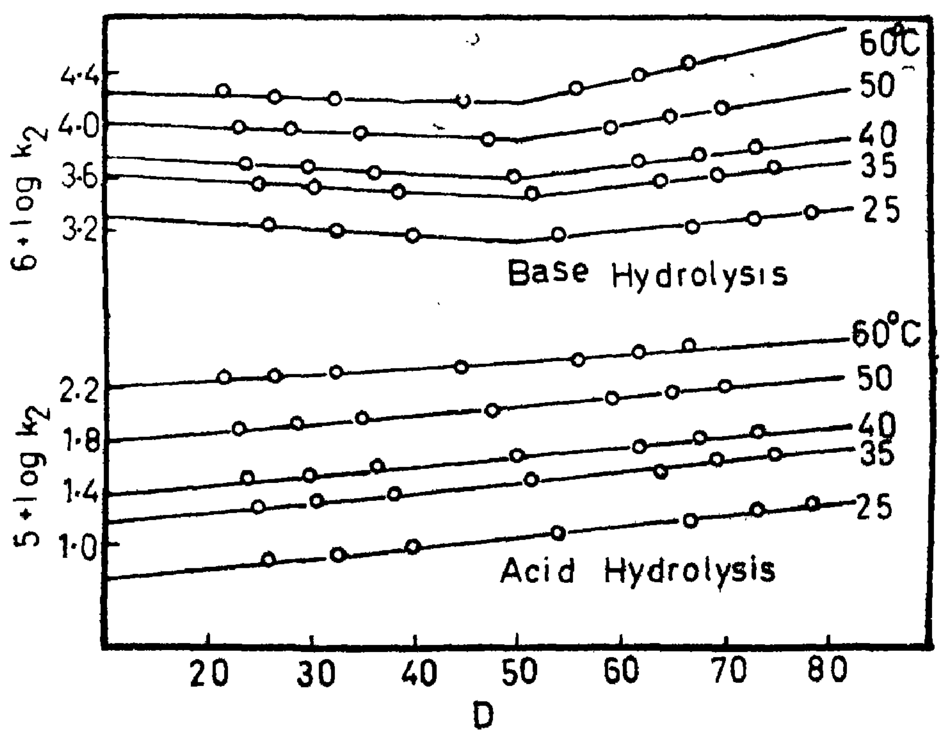


Fig. 1. Influence of dielectric constant on reaction rate.

mined[9] at different temperatures (Table 3). These were used to calculate the refined values of distances of closest approach for the activated complexes ($a_{\neq}$) at chosen values of D (10, 20, 40, 60 and 80). The

TABLE 3—VALUES OF k′ (in liter/mole/sec).

Temperature	25°	35°	40°	50°	60°
$5+\log k'_a$	0.679	1.132	1.828	1.731	2.159
$5+\log k'_b$	2.830	2.668	2.811	3.102	3.889

results are given in Table 2. It can be seen that the values of $a_{\neq}$ decrease with progressive addition of isopropanol. This is in agreement with the fact that successive additions of any organic solute must obviously disrupt the three-dimensional hydrogen-bonded structure of water and cause stronger interactions between the solvent molecules than occur in pure water. As a result, the reacting species might become closer to each other and so the distance of closest approach should be decreased.

However, the $a_{\neq}$ values are reasonable and may account for the solvation of the activated complex. Also they give an idea about the extent of solvation. The $a_{\neq}$ value is equal to, considering the mechanism of the reaction which is given below, the radius of the activated complex plus the radius of a water molecule.

Considering the hydration number for each of the hydrogen ion (4) and the hydroxide ion (3), one should expect large separation between the reactants in the transition state in the case of acid hydrolysis. Actually, the $a_{\neq}$ values were found to be higher in acid hydrolysis than that in base hydrolysis.

It is noteworthy that the radius of the activated complex in the acid or base hydrolysis of carboxylic amides of simple structure in aqueous-organic solvents seems to be almost independent of temperature and increases with increase in the dielectric constant and is, in general, dependent on the amide or the medium. This generalisation can be considered in the light of our results for formamide[1] and acetamide[3,4,7,9,10] hydrolysis in aqueous-organic solvents.

Solvent Composition Effect on Reaction Rate

In reactions in mixed solvents specific interactions of the solvent with the reactants and with the transition state can be of major importance in controlling reaction rate. Properties of the solvent alone do not necessarily predict the reaction rate and generalisation involving the structure of water also have no predictive value[11].

The variation of reaction rate with solvent composition, at constant acid or base concentration, may be ascribed primarily to changes in the solvent system through the equilibrium[1,12]

$$(H_2O)_sI + nS \rightleftharpoons nH_2O + (H_2O)_{s-n}S_nI$$

where I stands for a H_3O^+ or OH^- ion, involving substitution of water by the organic solvent molecules in the ion clusters by a multi-step solvation mechanism[12]. Therefore, the number of free water molecules increases on progressive addition of isopropanol and this plays an important role in the dependence of reaction rate on solvent composition. Also, the ratio ($a_{hyd\ I}/a_{solv\ I}$) will be directly proportional to $(a_w/a_s)^n$, and the reaction rate should be dependent on each of these two terms.

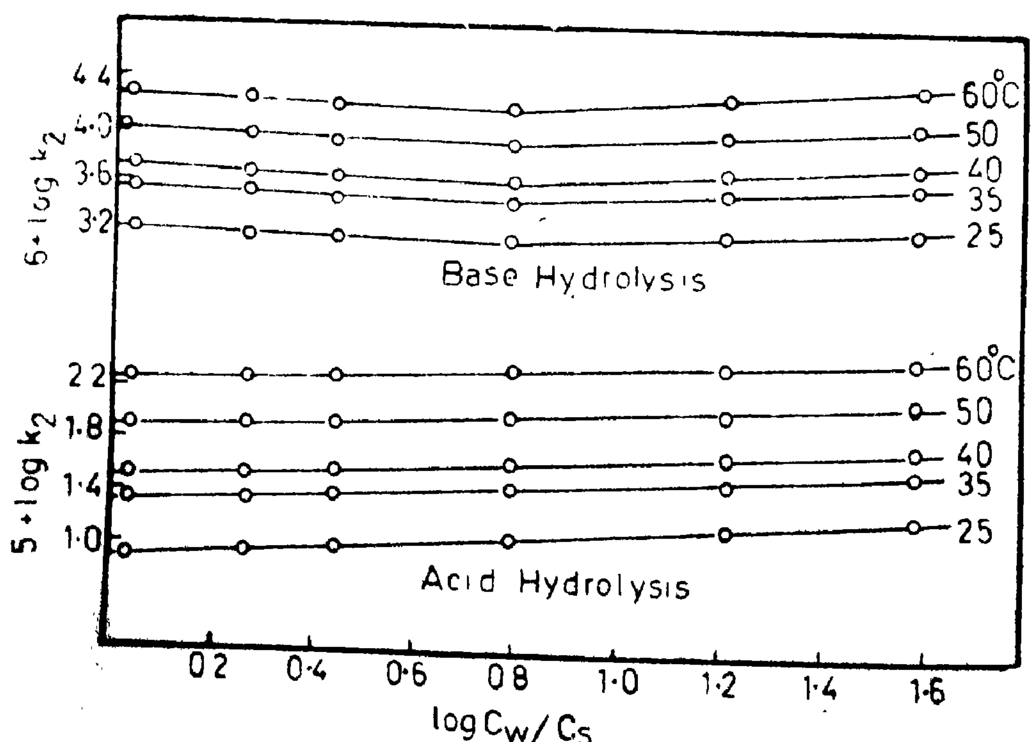


Fig. 2. Dependence of reaction rate on solvent composition.

In absence of the activities data for solutions of the binary alcohol-water mixtures, the values of molar concentrations may be used. It is reasonable to expect that the variation in the ratio C_w/C_s with solvent composition, in solutions of fixed acid or base concentration, is directly proportional to the variation in the a_w/a_s ratio. This may be actually true since the rate constants of the reactions were always determined under a constant ionic strength ($u=0.1$). However plots of log k_2 against log C_w/C_s gave good straight lines (Fig. 2), in acid hydrolysis and two linear portions corresponding to isopropanol- and water-rich mixtures in base hydrolysis, indicating the operation of the above equilibrium.

The dependence of reaction rate on water concentration (mole/liter) was also illustrated by a plot of log k_2 against log C_w. Two linear portions were obtained corresponding to water- and isopropanol-rich mixtures in acid and base hydrolysis. The slopes of these lines varied with temperature and amounted to 1.4-1.2 and 0.48-0.34 in the acid hydrolysis, and 1.10-1.90 and 0.21-0.31 in the base hydrolysis, at 25-60° respectively. These slopes, as generally known, represent the number of water molecules involved in the formation of the activated complex. The rate is thus proportional to the concentration of water in agreement with the expected bimolecular mechanism.

Solvation Effects and Activation Parameters

The increase of activation energy with successive addition of the organic solvent may be due to solvation of the activated complex to a less extent than of the reactants. However, the enthalpy ($\Delta H^{\neq}$) and entropy ($\Delta S^{\neq}$) of activation could be more sensitive indicators of effects of solvent structure than the rate constant directly[11]. The activation parameters were calculated and are listed in Table 4.

In the acid hydrolysis the enthalpy of activation increases gradually with increasing isopropanol content, whereas it decreases in base hydrolysis in the same direction. This behaviour may be a direct consequence of the variation of the isocomposition activation energy with the dielectric constant.

The free energy of activation, $\Delta F^{\neq}$, increases also gradually with increasing isopropanol content in acid hydrolysis, whereas it increases slightly at first and then decreases also slightly by further successive addition of the solvent in base hydrolysis. This weak dependence is due largely to the general linear compensation between the enthalpy and entropy of activation for a given temperature. According to the theory of absolute reaction rates, an increase in $\Delta F^{\neq}$ is indicative of the solvation phenomena[3,4]. This agrees with the observed increase of energy of activation in the same direction. Therefore, solvation is expected to be more pronounced in presence of isopropanol.

A major determinant of $\Delta S^{\neq}$ for reaction in solution is solvation change between reactants and

TABLE 4—THERMODYNAMIC PARAMETERS OF THE ACTIVATED COMPLEX
($\Delta F^{\neq}$ and $\Delta H^{\neq}$ in Kcal/mole, $\Delta S^{\neq}$ in Cal/mole/degree)

iso-Propanol wt %		7.95	16.25	84.08	53.49	64.32	75.06
				I—*Acid Hydrolysis*			
25°	$\Delta F^{\neq}$	22.58	22.71	22.84	22.93	28.00	28.05
	$\Delta H^{\neq}$	15.47	15.84	16.83	16.68	16.94	17.16
	$-\Delta S^{\neq}$	23.84	23.06	21.81	20.94	20.84	19.78
35°	$\Delta F^{\neq}$	22.82	22.97	23.03	28.16	23.22	28.26
	$\Delta H^{\neq}$	15.45	15.82	16.31	16.66	16.92	17.14
	$-\Delta S^{\neq}$	23.94	23.20	21.83	21.06	20.46	19.85
40°	$\Delta F^{\neq}$	22.94	28.08	23.14	28.25	23.33	28.36
	$\Delta H^{\neq}$	15.44	15.81	16.30	16.65	16.90	17.18
	$-\Delta S^{\neq}$	23.97	23.23	21.85	21.09	20.51	19.87
50°	$\Delta F^{\neq}$	23.17	23.31	28.39	23.47	28.52	28.55
	$\Delta H^{\neq}$	15.42	15.78	16.28	16.63	16.88	17.11
	$-\Delta S^{\neq}$	23.99	23.28	21.99	21.15	20.53	19.92
60°	$\Delta F^{\neq}$	23.41	23.54	23.60	23.66	28.72	28.76
	$\Delta H^{\neq}$	15.39	15.76	16.25	16.61	16.86	17.09
	$-\Delta S^{\neq}$	24.05	23.32	22.03	21.19	20.58	19.99
				II—*Base Hydrolysis*			
25°	$\Delta F^{\neq}$	21.18	21.27	21.35	21.33	21.31	21.24
	$\Delta H^{\neq}$	13.44	13.07	12.99	12.92	12.85	12.76
	$-\Delta S^{\neq}$	25.96	27.50	28.05	28.22	28.37	28.44
35°	$\Delta F^{\neq}$	21.39	21.55	21.64	21.62	21.59	21.52
	$\Delta H^{\neq}$	18.42	18.05	12.97	12.90	12.88	12.74
	$-\Delta S^{\neq}$	25.86	27.60	28.14	28.30	28.43	28.50
40°	$\Delta F^{\neq}$	21.57	21.70	21.79	21.77	21.74	21.66
	$\Delta H^{\neq}$	13.41	13.04	12.96	12.89	12.82	12.73
	$-\Delta S^{\neq}$	26.06	27.66	28.19	28.36	28.50	28.52
50°	$\Delta F^{\neq}$	21.83	21.98	22.00	22.07	22.03	21.94
	$\Delta H^{\neq}$	13.39	13.02	12.94	12.87	12.80	12.71
	$-\Delta S^{\neq}$	26.12	27.75	28.31	28.48	28.57	28.59
60°	$\Delta F^{\neq}$	22.10	22.26	22.38	22.35	22.32	22.22
	$\Delta H^{\neq}$	13.39	13.00	12.92	12.85	12.78	12.69
	$-\Delta S^{\neq}$	26.21	27.81	28.40	28.52	28.61	28.62

transition state. The incorporation of solvent into the transition state entails a loss of entropy. The entropy of activation varies with solvent addition in a non-linear manner. This behaviour indicates specific solvation[18] and hence a non-random distribution of the solvent molecules. The sudden variation of the entropy of activation noticed at about 34 wt % of isopropanol in the base hydrolysis may reflect the variation of reaction kinetics with solvent composition.

Medium Effects on Reaction Rate

The correlation between the rate of formamide hydrolysis and medium effects[14] has also been investigated in isopropanol-water mixtures. This correlation involves a linear dependence of the rate function L ($L = \log k_{obs} - pK_w$, where k_{obs} is the observed rate constant and k_w is the water ionisation constant) on the logarithm of the molar concentration of the water which is present as a component of the solvent system ($\log C_w$). On the other hand, it was pointed out[1] that the variation of the reaction rate may be determined by the variation of the water ionisation constant with water concentration of the solvent system. This conclusion can also be proved by plotting the rate function L versus $\log C_w$, at constant temperature, where very good straight lines with positive slopes (n) were obtained (Fig. 3). The slopes of the lines obtained amounted to $n_a = 3.22$ and $n_b = 4.01$ for the acid and base hydrolysis of formamide, in isopropanol-water mixtures at 25°, respectively.

Here again we find that $n_b = n_a + 1$. This should be expected since the value of n could be looked upon as the change in number of solvated water molecules in passing from reactants to the transition state in the rate determining step[14], and the H^+ or OH^- ion, in aqueous medium, is hydrated by four or three water molecules respectively. The values of the water ionisation constant in isopropanol-water mixtures were obtained at 25°, by interpolation, from the recently published data[15]. Unfortunately, their values at temperatures other than 25° were not reported in the literature. However, it is evident[1] that the n values are almost independent on temperature.

These results lend also further evidence to the validity of the correlation between the reaction rate and medium effects through the water ionisation constant and therefore Elsemongy's hypothesis[14] may be generally applicable.

Solvent Effect on Reaction Mechanism

The study of formamide hydrolysis in isopropanol-water mixtures was also made in a wider temperature range (25-60°) so as to examine the effect of temperature on the mechanism of the reaction. Successive addition of isopropanol alters the rate without influencing the mechanism and so the mechanism is the same for the different solvent compositions.

These data are consistent with our previously reported mechanisms for the acid[6] and base[7] hydrolysis of amides in aqueous-organic solvents. The analogies between the kinetic behaviour of formamide in acidic and basic isopropanol-water mixtures and that in acidic and basic dioxane-water mixtures[1] support our previous proposed mechanisms. Other evidences for these bimolecular mechanisms are the large negative values of the activation entropy and the values of energy of activation together with the

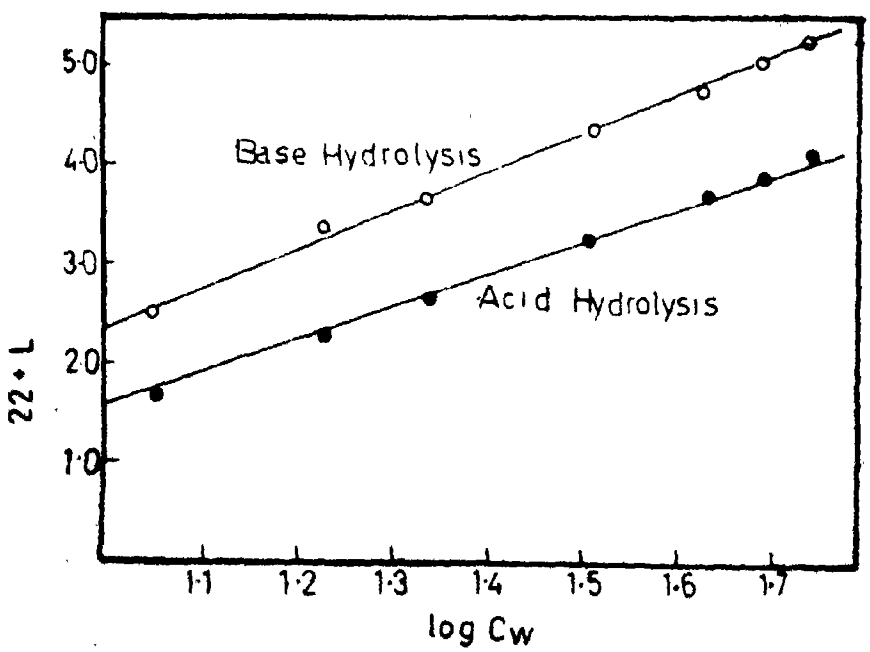


Fig. 3. Rate function and water concentration.

values of the frequency factor. These values are in excellent agreement with our previous proposed bimolecular mechanisms and thus they lend further support to the validity of these mechanisms.

Kinetics of Formamide Hydrolysis in Aqueous-Organic Solvents

Comparison of the kinetics of hydrolysis of formamide in isopropanol-water mixtures and in other aqueous organic mixed solvents[1,16] (dioxane- and n.propanol-water mixtures) might therefore yield information about the role of the solvent. In the acid hydrolysis of formamide the velocity constant decreases with progressive addition of dioxane or n.propanol and then increases passing through a minimum at concentrations characteristic of the organic solvent (50 wt % of dioxane and 34.5 wt % of n.propanol). On the other hand, in the base hydrolysis, the rate decreases in presence of dioxane and n.propanol. The reverse is observed here in isopropanol-water mixtures.

In acid hydrolysis, the reaction rate decreases in the order : dioxane>n.propanol>isopropanol. In base hydrolysis the reaction rate first decreases in the order : n.propanol>isopropanol>dioxane, then the rate increases on progressive addition of isopropanol. However, the reaction rate is generally much higher than that in acid hydrolysis.

These results may be clarified in the light of Oakenfull suggestion[11] that addition of the organic solvent might change the rate-determining step. The organic solvent molecule is more tightly bound in the transition state for formation of the intermediate than in the transition state for breakdown to products. Consequently the transition state for formation is the more polarizable and hence the more stabilized by addition of the organic solvent. Addition of the organic solvent would therefore tend more to increase the rate of formation of the intermediate than its rate of breakdown to products and large concentrations of the organic solvent would change the rate-determining step. This explanation is supported by the sharpness of the sharp change of variation of log k_a with D or with log C_w/C_s at concentrations characteristic of the organic solvent.

On the other hand, previous studies have shown that the N- and O-protonated amides are in equilibrium and that the concentration of N-protonated species increases with the electron-withdrawing character of the substituent on the nitrogen atom[4,17]. It was also shown that the equilibrium is solvent-dependent and that the concentration of N-protonated amide varies in the same way as the rate profile.

Recently a kinetic study, based on a reaction mechanism in which water attacks N-protonated conjugate acid in the rate-determining step, has been successfully carried out for the acid hydrolysis of amides. Thus the relative rates of hydrolysis can, however, be readily explained if one considers the N-protonated form to be kinetically favourable[4,18]. As the organic solvent concentration is increased the activity of water decreases simultaneously and, when this effect becomes more important than the increase in protonated intermediate, the rate of reaction decreases.

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Activity Coefficients in the Adsorbed Phase

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Activity coefficients of benzene and acetic acid at 20° on the surface of tin oxide gel have been calculated making use of Everett's model of adsorption. The values vary from 1.031 to 0.8710 for acetic acid and from 0.9729 to 0.0003 for benzene upto 0.7 mole fraction of acetic acid after which phase separation starts, making calculations impossible. The values reveal strong intermolecular forces of attraction in the adsorbed phase.

SURFACE activity coefficients in a solid-liquid interface denote the escaping tendencies of the components of a liquid mixture from the surface of a solid just as activity coefficients in a liquid-vapour interface represent the escaping tendencies of the components to go into the vapour phase. The values in these two interfaces are likely to be different because surface forces besides the molecular forces play their role in the solid-liquid interface. Blackburn et al[1] investigated the surface activity coefficients of components of a number of binary liquid mixtures on the surface of carbons and graphite. They used Elton's convention[2] that surface activity and hence its surface activity coefficient is 1 when its mole fraction is 1 although this convention is open to criticism in the case of partly miscible liquid mixtures. They further assumed that the activity of a component in the solid and the liquid phase is the same at equilibrium. Lu and Lama[3] calculated the surface activity coefficients of benzene and cyclohexane in adsorption from this liquid mixture on silica gel. They found that activity coefficients were more than unity for both the components over the whole concentration range. It was thought of interest to take acetic acid-benzene mixture for such investigation as this mixture presents a highly non-ideal system in the liquid phase. The absorbent was tin oxide gel with the surface area of 160 $m^2/_g$ whose method of preparation has been reported earlier[4,5]. One gram of the solid was treated with 10 ml of the mixture of varying concentrations and was shaken occasionally for 24 hrs. The solutions were analysed refractometrically, the blank solutions also having been treated similarly. The temperature of adsorption was 20°. Mole fractions in the adsorbed phase were estimated by using Everett's equations[6]

$$\frac{x_1 x_2}{n_0 \Delta x_2/m} = \frac{m}{n^\sigma} \left(x_2 + \frac{1}{k-1}\right) \quad \ldots\ldots\ldots(1)$$

and $$n_0 \Delta x_2/m = n_2^\sigma \quad (x_2^\sigma - x_2)/m \quad \ldots\ldots\ldots(2)$$

where x_1 and x_2 stand for the mole fractions of

TABLE

CALCULATION OF SURFACE ACTIVITY COEFFICIENTS OF BENZENE(1) AND ACETIC ACID(2) IN THE ADSORBED PHASE ON TIN OXIDE GEL

	Mole fraction of acetic acid x_2 in the liquid					
	0.1	0.2	0.3	0.4	0.6	0.7
x_1	0.9	0.8	0.7	0.6	0.4	0.3
$x_2 r_2$	0.045	0.075	0.110	0.140	0.2	0.235
$x_1 r_1$	0.955	0.925	0.890	0.860	0.8	0.765
x_2^σ	0.486	0.7	0.786	0.830	0.843	0.886
x_1^σ	0.514	0.3	0.214	0.170	0.157	0.114
$\log \frac{x_1^\sigma x_2 r_2}{x_2^\sigma x_1 r_1}$	−1.3024	−1.4590	−1.4730	−1.4771	−1.3320	−1.4081
$x_1^\sigma \log \frac{x_1^\sigma x_2 r_2}{x_2^\sigma x_1 r_1}$	− .6694	− .4376	− .3152	− .2510	− .2091	− .1599
$\int_0^{x_1^\sigma} \log \frac{x_1^\sigma x_2 r_2}{x_2^\sigma x_1 r_1} dx_1^\sigma$	− .683	− .373	− .253	− .178	− .163	− .100
r_2^σ	1.0310	0.8618	0.8666	0.8458	0.8995	0.8710
r_1^σ	0.9729	0.4452	0.1408	0.0151	0.0462	0.0003

benzene and acetic acid respectively in the liquid phase. Δx_2 is the change in the mole fraction of acetic acid when m gram of the solid is equilibrated with n_0 moles of the liquid mixture. n^σ and x_2^σ represent the total number of moles of the components and the mole fraction of component 2 in the adsorbed phase. k is the distribution constant. Surface activity coefficients were then determined by using Everett Equation[7].

$$ln\ r_2^\sigma = x_1^\sigma\ ln\left(\frac{x_1^\sigma x_2 r}{x_2^\sigma x_1 r_1}\right) - \int_0^{x_1^\sigma} ln\ \left(\frac{\lambda_1^\sigma x_2 r_2}{x_2^\sigma x_1 r_1}\right) d\lambda_1^\sigma$$

For the calculation of surface activity coefficients, graphical integration which gives accurate values has been carried out. The activity coefficients in the liquid phase, r_1 and r_2 were calculated from the vapour-pressure data reported in the literature[8]. Since refractometry gives values correct up to three places of decimal, the error involved in the calculation of number of moles, mole fractions and activity coefficients in the adsorbed phase is negligible. The activity coefficient of acetic acid in the adsorbed phase varies from 1.031 to 0.8710 and that of benzene from 0.9729 to 0.0003. Calculations could be made up to 0.7 mole fraction of acetic acid as after that phase separation starts making calculations impossible. Thus the system presents a highly non-ideal picture in the adsorbed phase. It seems reasonable to say that there are strong intermolecular forces in the adsorbed phase which decrease the tendencies of the components to escape into the liquid phase.

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Environmental Influences on Adsorption of 1, 3 Dichloropropene by 'AKLI' Bentonite

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Investigations on the effect of time, pH, exchangeable cations, organic matter and temperature on the adsorption of telone on bentonite showed that a minimum period of 8 hours for hydrogen saturated and 10 hours for sodium saturated bentonite was required for completion of the process of adsorption. The adsorption of telone increased with a decrease in pH. The interaction was cation dependent and occurred mostly due to ion exchange. Organic matter in form of humic acid increased the degree of adsorption due to interaction of the telone molecule with organic matter. The process was temperature sensitive and decreased with a rise in temperature.

TELONE (1, 3-dichloropropene) is widely employed as a soil fumigant to combat the destructive action of plant parasitic nematodes and other soil organisms. In contact with soil colloid it is readily adsorbed. In recent communications the authors[1-3] proposed reaction mechanisms for its adsorption on acid and base saturated clays. Work by other investigators revealed that among several factors adsorption of pesticides on soil colloids is affected by *p*H, organic matter, type of cation on the clay surface, temperature and molecular structure[4-9]. Since the phenomenon of adsorption influences the fate and behaviour of a pesticide in the soil system, and makes it possible to calculate proper pesticide doses and since adsorption itself is affected by environmental conditions, the aim of the present study was to investigate the influence of certain critical factors such as time, *p*H, exchangeable cations, organic matter and temperature on telone sorption by 'Akli' bentonite.

Experimental

The bentonite used in these studies was obtained from 'Akli' in Rajasthan. X-ray diffraction showed that it was mainly composed of montmorillonite. After removal of organic matter with hydrogen peroxide, the clay was dispersed and less than 2u fraction converted into chloride free sodium and hydrogen saturated forms by Aldrich and Buchanan's method[10]. The concentration of the suspensions was 11.0 g per litre. The cation exchange capacity of the bentonite was found to be 90 meq per 100 g.

For the investigation of the effect of time on telone adsorption, the experiments were conducted at the *p*H values of 6.9 in case of sodium saturated bentonite and 3.5 in case of hydrogen saturated bentonite in which eight samples of 10 ml of hydrogen and sodium saturated bentonite suspensions were treated with a constant amount of an alcoholic solution (2.5 ml of telone solution containing 10 g per litre) of telone. The mixtures were adjusted to a constant volume of 25 ml with alcohol and distilled water. The tubes were shaken at 28 $\pm 0.1°$ in a thermostatic water bath. Samples were drawn at intervals of 1, 2, 4, 6, 8, 10, 12, 16 and 20 hours respectively and centrifuged. The amount of telone remaining unadsorbed was then immediately estimated in the supernatant liquids using silver thiocyanate ferric alum method[11]. The results for the effect of time on the amount of telone adsorbed by hydrogen and sodium saturated bentonite are represented (Fig. 1).

For the investigation of the effect of *p*H on telone sorption, sodium saturated bentonite suspensions were treated with 0.1*N* HNO_3 and 0.1*N* NaOH respectively, to obtain the desired equilibrium levels of *p*H (2.0, 3.5, 5.0, 7.0, 8.5 and 10.0). The adsorption of telone was then studied at each of the above *p*H values as described below in case of exchangeable cations. The results are given in Fig. 1.

The adsorption of telone on hydrogen and sodium saturated bentonites was determined by taking 10 ml aliquots containing 110 mg of the appropriate clay in a large number of glass stoppered tubes and adding different amounts of an alcoholic solution (10 g per litre) of telone. The mixtures were diluted to 25 ml with alcohol and distilled water so that the alcohol content of the mixtures was minimum and the same in all cases. After intermittent shaking and standing for 12 hours at a temperature $28 \pm 0.1°$, their *p*H and conductance were recorded. The suspensions were then centrifuged. The supernatants showed the formation of chloride and residual telone in them. The chloride ions and the residual telone were estimated in the supernatants with and without refluxing the supernatants with N alcoholic KOH, using silver thiocyanate ferric alum method[11]. The difference gave the amount of telone remaining in the equilibrium liquid after adsorption. The amount of telone adsorbed was calculated from the amount of telone added and

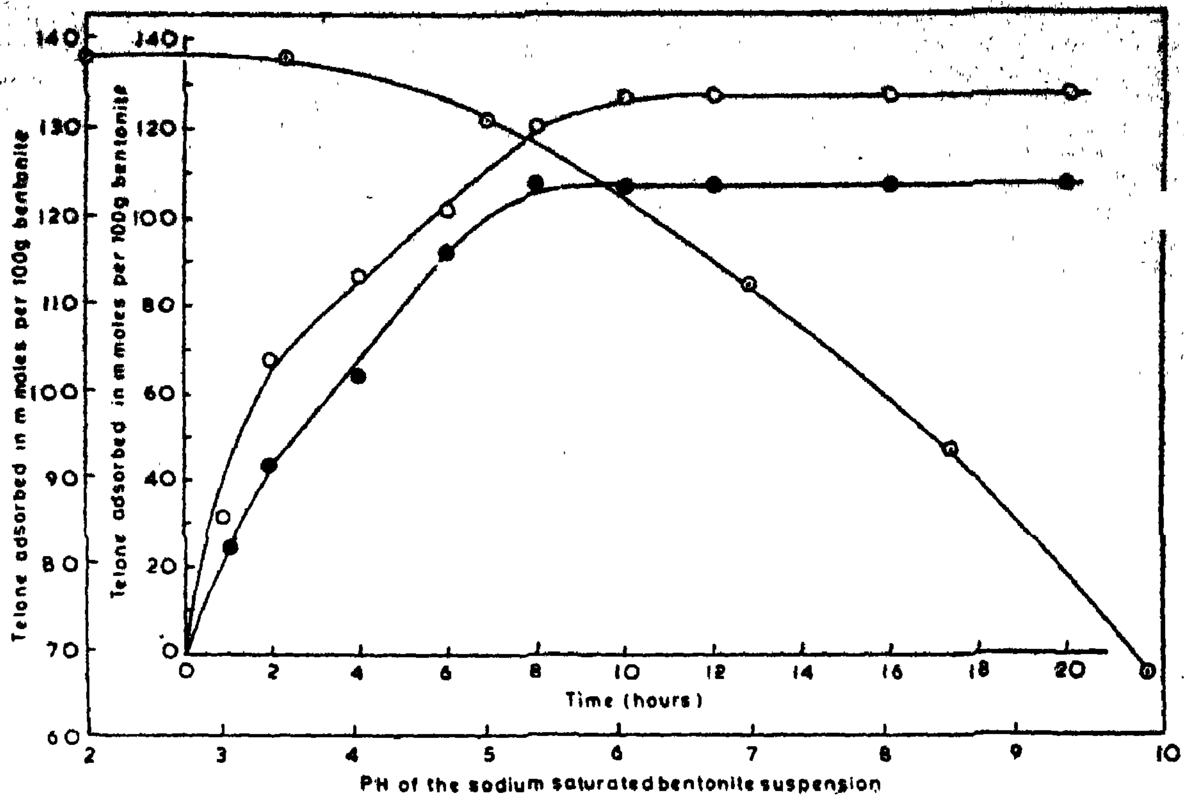


Fig. 1. Effect of Time and pH on Adsorption of Telone by Sodium and Hydrogen Saturated Bentonites

⊙ Sodium saturated bentonite
● Hydrogen saturated bentonite
○ Sodium saturated bentonite

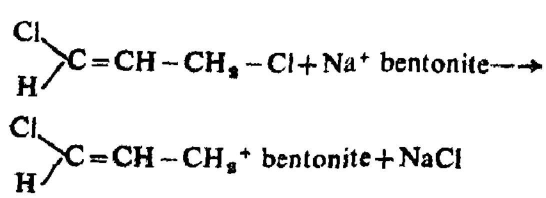
remaining after contact with clay. The results of adsorption and the pH and conductivity changes produced are represented in Figs. 3 to 4 respectively. For a study of temparature effect this experiment was also done at $42 \pm 0.1^{\circ}$.

The effect of organic matter on the adsorption of the nematocide was then examined by taking 10 ml aliquots of hydrogen and sodium saturated clay suspenions in glass stoppered tubes and adding 50 mg of humic acid in each case in the first set of experiments and 100 mg of humic acid in the second set and then adding varying amounts of 1% solution of telone to the suspensions as described earlier. The pH and conductometric variations produced during interaction of telone with hydrogen and sodium saturated bentonites in presence of humic acid were also recorded. The results of adsorption, pH and conductivity variations are reported (vide Figs. 3 to 4). The adsorption of telone on humic acid alone was also studied.

Results and Discussion

The effect of time on adsorption of telone is presented in Fig. 1. Adsorption slowly increased with time till the systems approached equilibrium at 8 hours in case of hydrogen saturated bentonite and 10 hours in case of sodium saturated bentonite. The slow adsorption of telone by bentonites appeared to be due to certain interactions which must be taking place between the pesticide and the lateral, planar and interior surfaces of the clay. A period 8 and 10 hours for hydrogen and sodium bentonites, respectively, appeared to be sufficient for attainment of equilibrium and for carrying out further adsorption experiments.

The effect of pH on the extent of adsorption of telone on bentonite is also illustrated in Fig. 1. In the range studied the adsorption continuously increased with a decrease in pH till it became almost constant below pH 3.5. The results were in agreement with the findings of many other workers who explained the increase in adsorption of pesticides with decreasing pH as being due to protonation of the molecule followed by adsorption. The reaction mechanism in our case was as follows :



At higher pH values this interaction did not occur to any appreciable extent. Whatever adsorption

occurred at higher *pH* values was due to van der Waals forces and was low[7]. These findings indicated that under natural conditions the rate of telone needed for nematocidal action in montmorillonite soils would vary with soil *pH*. Acidic soils with a lower *pH* will require larger doses of the chemical to overcome the increased rate of adsorption. This was in agreement with the results reported by Burnside and Behrens[12] on the phytotoxicity of simazine as affected by soil *pH*.

The results of adsorption of telone on hydrogen and sodium saturated bentonites are illustrated in Fig.2. The shapes of the isotherms[13] and the nature of *pH* and conductivity variations produced (Figs 2 to 4) during the interaction suggested a definite cation exchange reaction mechanism between telone and hydrogen and sodium saturated bentonites followed by penetration of the pesticide in the micropores as already discussed in an earlier publication of the authors[8]. To examine the effect of organic matter on the adsorption, the adsorption experiments were, however, redone to obtain similarity of conditions of experiments. The isotherms did not follow the Langmuir relation $C/x/m = \frac{1}{KB} + \frac{C}{B}$. From the shapes of adsorption isotherms (Fig.2, curves 1 and 2) it was clear that a

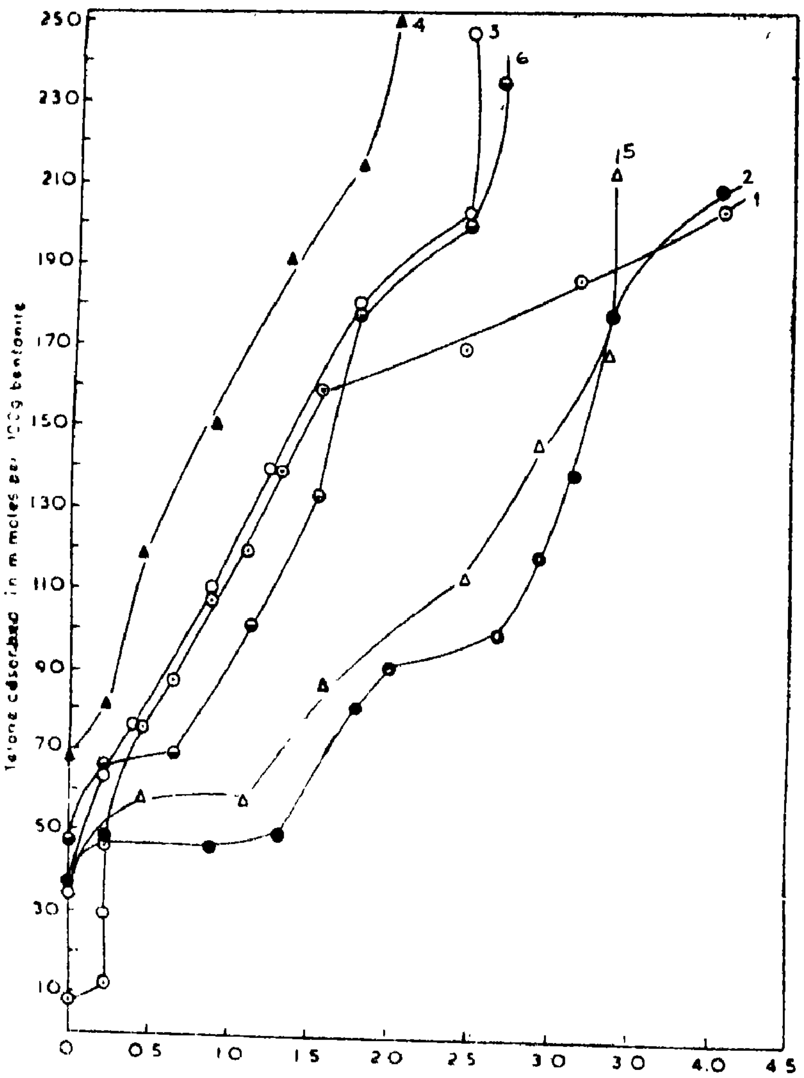


FIG 2. EFFECT OF EXCHANGEABLE CATIONS AND ORGANIC MATTER ON THE ADSORPTION OF TELONE BY SODIUM AND HYDROGEN SATURATED BENTONITES

⊙ Sodium saturated bentonite
○ 0.5% Humic acid + sodium saturated bentonite
▲ 1.0% Humic acid + sodium saturated bentonite
● Hydrogen saturated bentonite
△ 0.5% Humic acid + hydrogen saturated bentonite
◉ 1.0% Humic acid + hydrogen saturated bentonite

larger amount of telone was adsorbed on sodium saturated bentonite in the earlier stages as compared to hydrogen saturated bentonite. The nature of exchangeable cation on the bentonite surface was thus very important in determining the degree of adsorption of telone and the optimum dose for nematocidal action in soils. This deduction was in agreement with the findings of other workers[14,15] on the adsorption of organic pesticides on clays and soils.

The values obtained for the adsorption of telone on hydrogen and sodium saturated bentonites in presence of 0.5 and 1.0 per cent humic acid are given in Fig.2. An examination of the curves (Fig.2, curves 3 to 6) showed that bentonites acquired a higher capacity for adsorption in the presence of humic acid and it increased with an increase in the percentage of organic matter (Fig.2, curves 3 to 6). This suggested the possibility of an interaction between the organic matter present in bentonites and the nematocide. The humic acid is bound to interact with clays forming some kind of clay-organo-complexes. Hance[7] suggested that, in soil, clay and organic matter associate in such a manner that little of the clay mineral surface was available to pesticide molecules. On the other hand, Mortland[16] concluded from an investigation on a model system, that organic compounds in soil organic matter upon interaction with clay may facilitate and stabilise adsorption of pesticides beyond that observed in a purely inorganic clay system. Our data appeared to be in agreement with Mortland's suggestion. Thus humic acid on interaction with bentonites and present as a clay organo-complex may facilitate the adsorption of telone on the clays in soils.

In support of the above conclusion the results of adsorption of telone on humic acid alone were studied. The results of pH and conductivity variations during adsorption of nemotocide on humic acid indicated an interaction between telone and humic acid. Humic acids possessed functional groups such as phenolic hydroxyl, alcoholic hydroxyl and carboxyl groups which on dissociation could participate in exchange reactions[8]. The interaction between telone and the organic matter

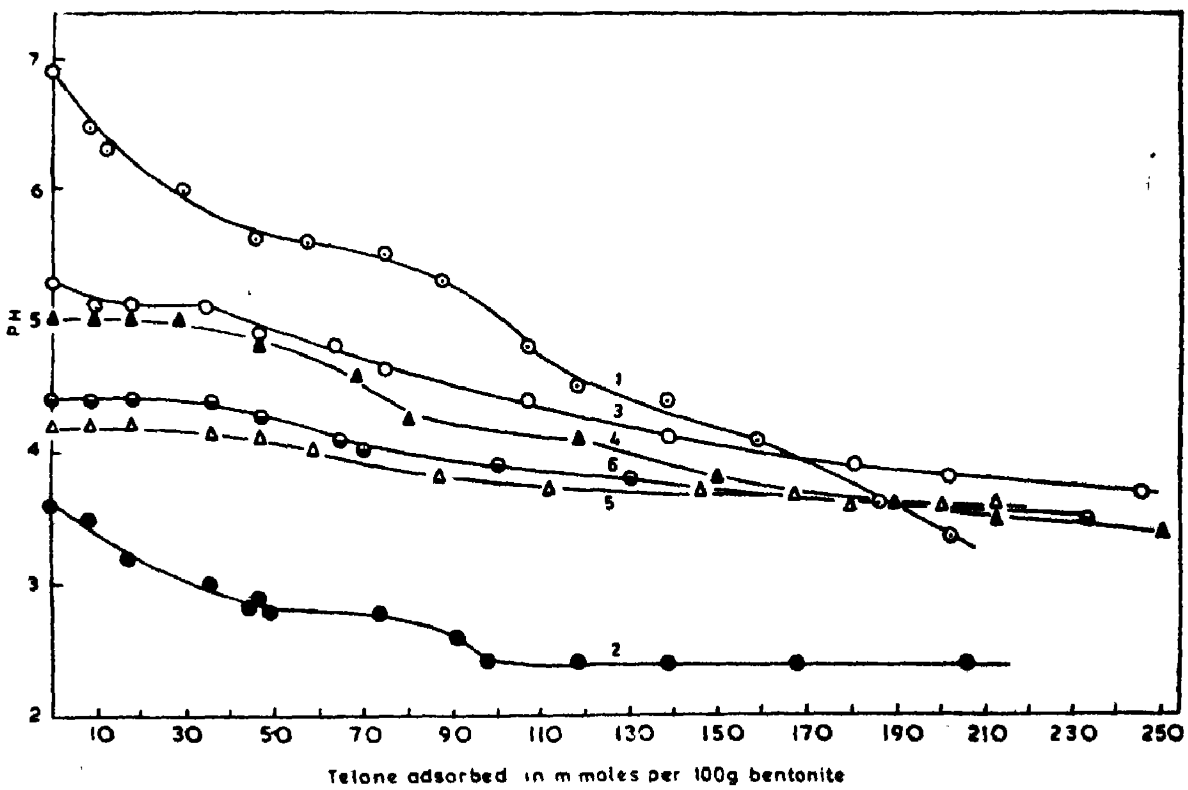


Fig. 3. Variation in pH with amount of telone adsorbed by Sodium and Hydrogen Saturated Bentonites and in presence of Organic matter.

⊙ Sodium saturated bentonite
○ 0.5% Humic acid + sodium saturated bentonite
▲ 1.0% Humic acid + sodium saturated bentonite
● Hydrogen saturated bentonite
△ 0.5% Humic acid + hydrogen saturated bentonite
⊖ 1.0% Humic acid + hydrogen saturated bentonite

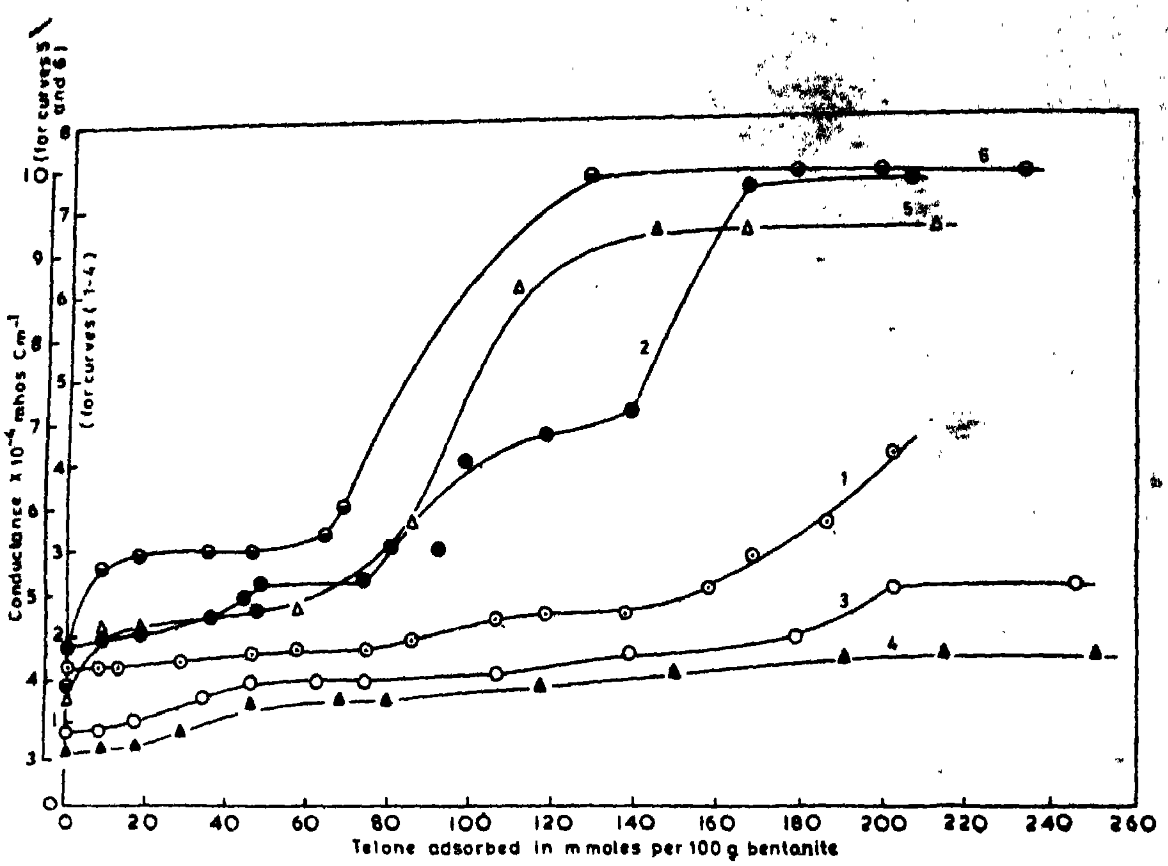


Fig. 4. Variation in Electrical Conductivity with amount of Telone adsorbed by Sodium and Hydrogen Saturated Bentonites and in presence of Organic matter.

○ Sodium saturated bentonite
○ 0.5% Humic acid + sodium saturated bentonite
▲ 1.0% Humic acid + sodium saturated bentonite
● Hydrogen saturated bentonite
△ 0.5% Humic acid + hydrogen saturated bentonite
◒ 1.0% Humic acid + hydrogen saturated bentonite

thus occurred by the following mechanism,

$$\underset{H}{\overset{Cl}{>}}C-CH-CH_2-Cl+ROH \rightarrow \underset{H}{\overset{Cl}{>}}C-CH-CH_2-OR+HCl$$

where R was the carboxyl, phenolic, alcoholic or hydroquinone group present in humic acid. This process increased the adsorption of the nematocide on hydrogen and sodium saturated bentonites in presence of humic acid.

The decrease in pH and a rise in electrical conductivity (Figs. 3 and 4) characteristically in the same manner as in the case of humic acid was as a result of the formation of HCl during the interaction of telone both with the organic matter, as indicated above, and with the Na- and H-bentonites as described earlier. The additive effect was responsible for an increased adsorption of telone on the clay-organo complexes. The results found support from the work of Khan[17] on the interaction of bipyridylium herbicides with organo-clay complex.

The effect of temperature on the adsorption of telone by sodium and hydrogen saturated bentonites at a pH value of 6.9 in case of sodium saturated bentonite and 3.6 in case of hydrogen saturated bentonite indicated a substantial effect of temperature on adsorption of telone on the sodium and hydrogen saturated bentonites. Over the entire range studied an increase in temperature resulted in a decrease in adsorption. This was in agreement with the general phenomenon observed in adsorption of pesticides on clays[18,19]. Adsorptive processes are exothermic and therefore an increase in temperature was followed by a decrease in adsorption as observed in our case. Soils in tropical regions will, therefore, need lower doses of the chemical for nematocidal action subject to control over other environmental factors as compared to soils in cold regions.

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Spectrophotometric Investigation of Ti(IV) Complexes with Benzohydroxamic Acid

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The extractive spectrophotometric measurements have revealed the formation of Ti(IV) complexes with metal to ligand ratios of 1 : 2 and 1 : 1 at acidities 4*N* and 8*N* HCl respectively. A rapid method for simultaneous solvent extraction and photometric determination of microamounts of titanium is described. The stability constants, stepwise as well as overall, of 1 : 2 and 1 : 1 complexes have been evaluated by graphical extrapolation methods following Yatsimirskii's and Leden's ideas. The analytical suitability of the reagent at different acid concentrations has also been investigated.

BENZOHYDROXAMIC acid (BHA) has been utilized[1] for the gravimetric estimation of titanium. BHA has also been used for the solvent extraction and photometric estimation of many metal ions[2-5]. It is reported that depending on the *p*H, iron(III) and vanadium(V) form different complexes[6,7]. Whether titanium also forms different complexes at varied acidities, the present investigation is undertaken taking advantage of the extractability of titanium complexes into water immiscible solvents. The present paper records simultaneous solvent extraction and spectrophotometric determination of microamounts of titanium with BHA. At 4*N* and 8*N* HCl medium 1 : 2 and 1 : 1 complexes are formed. This has been established by measuring absorbances of the yellow coloured solutions at 390 nm following the continuous variation[8,9] and molar ratio[10] methods. The stepwise and overall formation constants of the complexes have been evaluated by different methods[11-14] and compared. The suitability of the reagent for analytical determination of titanium in presence of diverse ions has been discussed.

Experimental

Reagents and Solutions : A stock solution of titanium (2.18 mg/ml) was prepared from A. R. Potassium titanyl oxalate and was standardised[15]. The reagent, BHA, was prepared by the method of Blatt[16]. Standard reagent solutions of desired strength in A. R. isoamyl alcohol were used.

Other chemicals and solvents used in all spectrophotometric measurements were of A. R. or spectrograde quality.

Apparatus : Spectrophotometric measurements were carried out on a Hilger Uvispek spectrophotometer with matched 1 cm. glass cells.

Extraction Procedure : For the sake of recording absorption spectra and the effect of acid and reagent concentration, an aliquot of titanium solution ($8.352\times10^{-5}M$) was taken into a 100 ml separatory funnel and adjusted to desired acidity. To 15 ml of the aqueous phase was added a desired amount of reagent solution (0.15 *M*) in isoamyl alcohol, the volume of the nonaqueous phase always being maintained equal to that of the aqueous phase. After shaking thoroughly the aqueous and nonaqueous phase for 5 minutes to reach equilibrium, the yellow coloured nonaqueous layer was drained out in a 50 ml beaker and dried over anhydrous sodium sulphate. The aqueous phase was subjected to extraction with a further 5 ml of isoamyl alcohol. The combined extract after drying over sodium sulphate was diluted to 25 ml with isoamyl alcohol. Equimolar solutions of titanium and the reagent ($1.823\times10^{-3}M$) were utilised, by incorporating two sets of complementary solutions, the volume being 6 ml and 3 ml respectively, to find the metal to ligand ratios by the methods[8-10] mentioned. The absorbances of the yellow coloured complexes were measured at 390 nm against the reagent blank.

Results and Discussion

Absorption spectrum : The absorbance spectra of the complex solutions, measured in the wavelength region 350-450 nm shows gradual decrease in value. As the absorbance value of the reagent solution was found appreciably low around 390 nm, all absorbance measurements were done at 390 nm against the reagent blank. Fig. 1 represents the spectral curves of Ti-BHA complexes at 4*N* and 8*N* HCl against reagent blank and of BHA against solvent blank. BHA has same absorption at 4*N* and 8*N* HCl.

Effect of reagent concentration : The metal was extracted at 4*N* and 8*N* HCl respectively with varying concentrations of the reagent. The results indicate that a single extraction with 8 ml of 0.15*M*

* A portion of this work was submitted to the Jadavpur University in 1974 in partial fulfilment of the requirements of the Ph. D. degree in Chemistry.

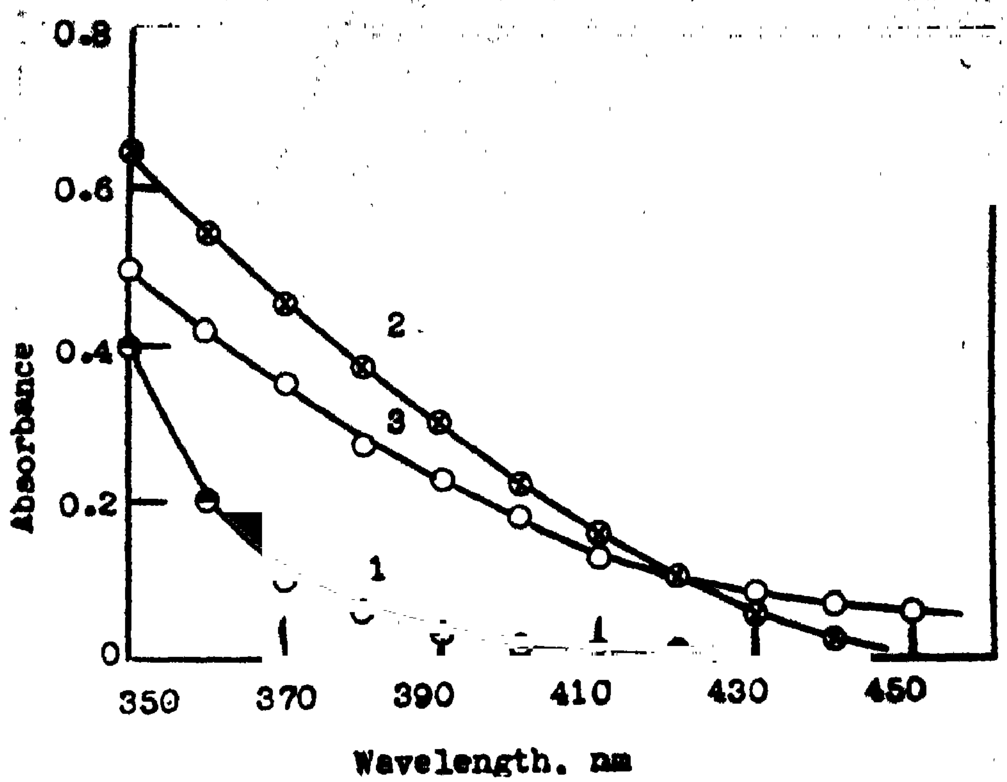


Fig. 1. Absorbance curves of Ti-BHA Complexes.

1. ⊖ [R] = 0.15*M*, Acidity = 4*N* and 8*N* HCl.
2. ⊕ [M] = 1.67×10^{-4} *M*, [R] = 0.15*M*, Acidity = 4*N* HCl.
3. ○ [M] = 8.8502×10^{-4} *M*, [R] = 0.15*M*, Acidity = 8*N* HCl.

BHA was quite adequate for quantitative extraction. The colour of the complexes was found to be stable for about 2½ hours.

Effect of acid on composition of the complexes : Titanium complexes of BHA are extractable into isoamyl alcohol from 2*N* to 9*N* HCl. The colour of the complex solution is yellow. Absorbances of different sets of complementary solutions (both Job's[8,9] and molar ratio[10] method), measured at 390 nm revealed that the complexes are predominantly 1 : 2 in the acidity range 2-4*N* and 1 : 1 in 7.5-9*N* HCl. For other measurements, 4*N* and 8*N* acids were used for 1 : 2 and 1 : 1 metal-ligand systems. The results are depicted in Fig. 2 and Fig. 3.

Calibration curve, optimum range and photometric error : The calibration curve for the complex systems were constructed by measuring the absorbances of different amounts of titanium, extracted according to given procedure, at 390 nm against the reagent blank. Beer's law was obeyed over the concentration ranges (1-14) ppm and (1-11) ppm at acidity 4*N* and 8*N* HCl respectively.

The optimum concentration with the highest accuracy, evaluated from Ringbom's[17] curves were (5-13) ppm and (3-10) ppm at respective acidities.

The relative analysis error per one percent absolute photometric error, calculated according to Ayre's equation[18] was 2.8 and 2.72 at the respective acidities.

Molar absorptivity and sensitivity : The molar absorptivity of the complexes at acidity 4*N* and 8*N* HCl, calculated from Beer's law data are $(1.48 \pm 0.08) \times 10^3$ and $(2.32 \pm 0.02) \times 10^3$ respectively. The sensitivity, according to Sandell[19] at the respective acidities are 0.031 and 0.021 μg per cm².

Effect of diverse ions : The effect of diverse ions on the absorbance of Ti(IV)-BHA complexes at 4*N* and 8*N* HCl were investigated at 390 nm. Moderate amounts of ions, commonly associated with titanium were found to be tolerable. The ions having strong interference include Fe(III), Ce(IV), V(V), Mo(VI) and W(VI).

Formation constants of the complexes : Stepwise formation constants for 1 : 2 system was calculated following Yatsimirskii's[11] and Leden's[12] method. The equilibrium ligand concentrations and the degree of complex formation were calculated from Beer's law. The construction of suitable functions and their evaluation was made in the manner stated earlier[14] from data in Tables 1 and 2. The values for overall stability constants were also obtained by

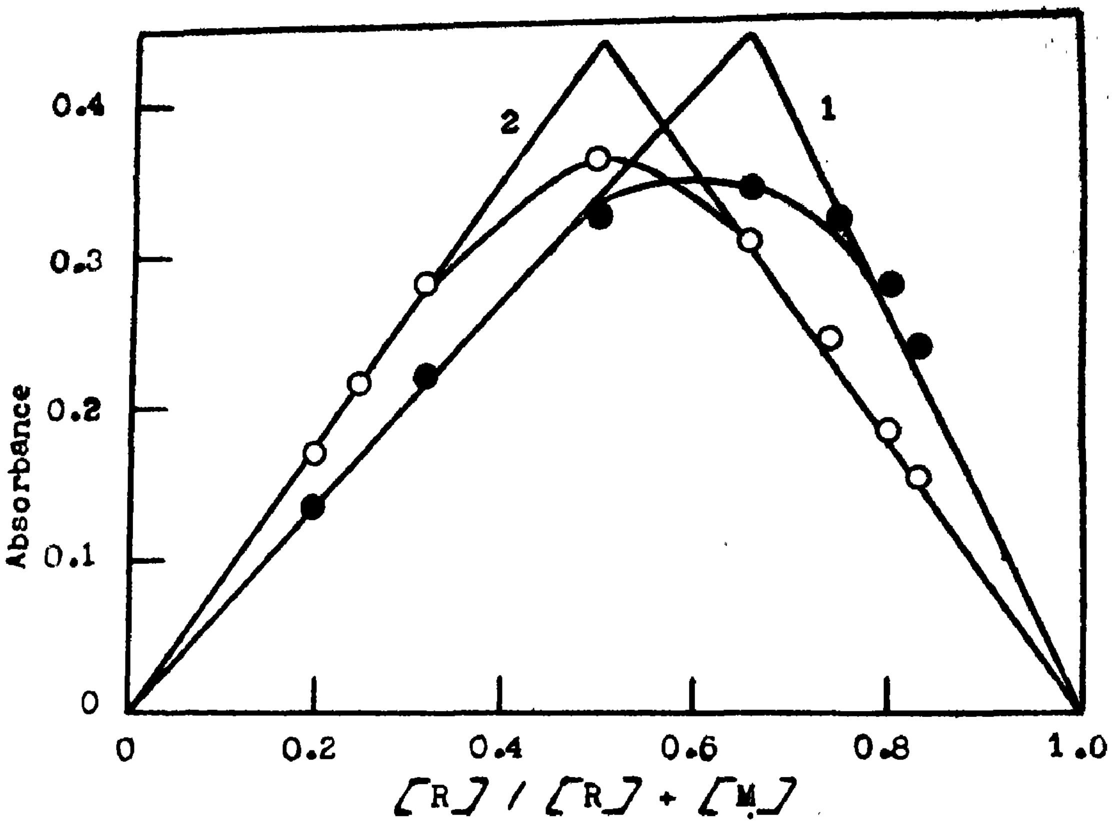


Fig. 2. Job's plot.
1. ● Ti-BHA Complex at $4N$ HCl
2. ○ Ti-BHA Complex at $8N$ HCl
$[M]=[R]=1.823\times10^{-3}M$ in each case.

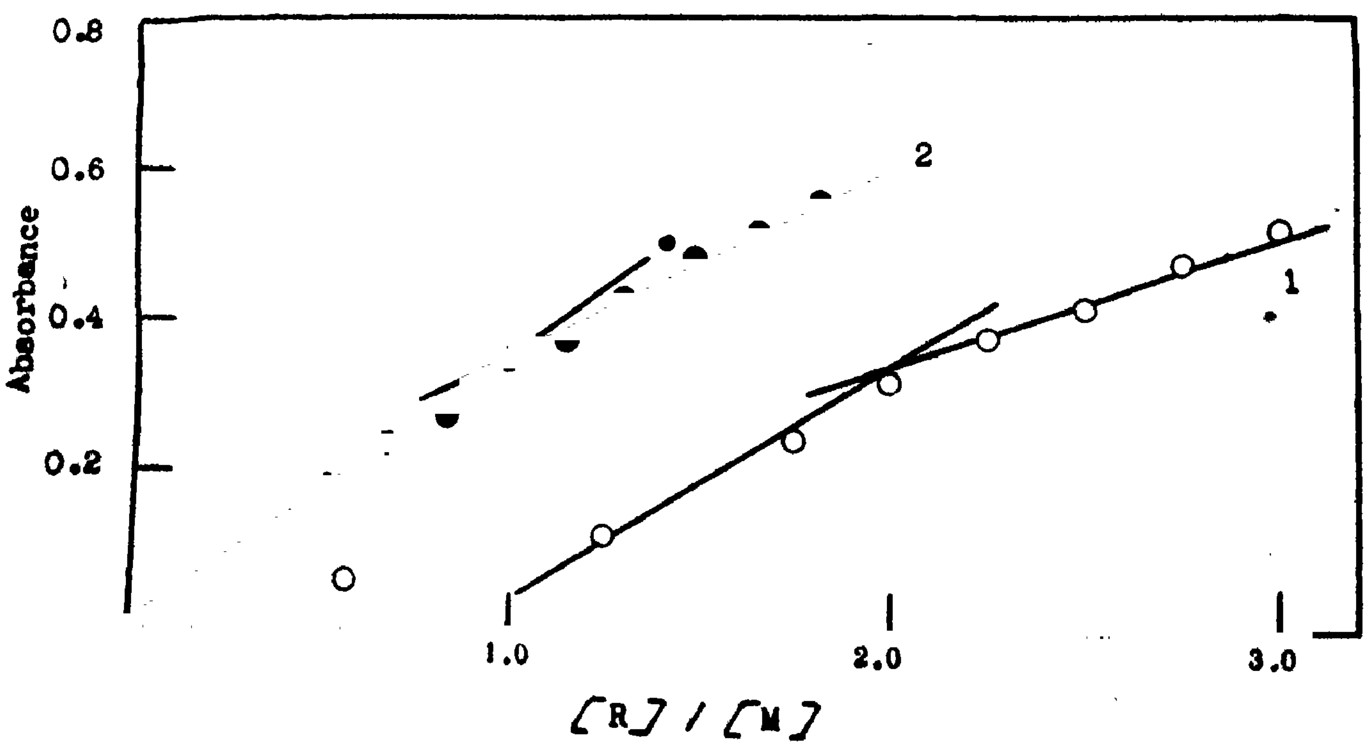


Fig. 3. Molar ratio-method.
1. ○ Ti-BHA Complex at $4N$ HCl. Metal taken = 2ml
2. ● Ti-BHA Complex at $8N$ HCl. Metal taken = 1.5 ml.
$[M]=[R]=1.823\times10^{3}M$

TABLE 1—YATSIMIRSKII'S METHOD

Ti-benzohydroxamic acid complex

[Metal] = [Reagent] = $1.828 \times 10^{-3} M$; [Metal]: [Reagent] = 1 : 2, Solvent = Isoamyl alcohol
Metal taken = 2 ml of $1.828 \times 10^{-3} M$; Final volume = 25 ml ; Time of Extraction = 5 mins.
Absorbance for metal conc. $2.087 \times 10^{-4} M$ = 0·305
Wavelength for measurement = 390 nm.

Solution	Total ligand conc. M/lit. ($C_L \times 10^3$)	Absorbance	Equilb. Ligand conc. M/lit. ($L \times 10^3$)	Molar Extinction co-efficient ϵ ($\times 10^{-3}$)	Y ($\times 10^{-3}$)	f_1 ($\times 10^{-4}$)	f_2 ($\times 10^{-7}$)	g
1	1.8280	0.125	1.6518	0.8574	0.6063	—	—	−0.8908
2	2.5528	0.250	2.2106	1.7160	0.4523	—	—	−1.0090
3	2.9168	0.325	2.4718	2.2290	0.4044	0.9018	0.5129	−0.9940
4	3.2814	0.380	2.7612	2.607	0.3621	0.9441	0.6125	−1.007
5	3.6460	0.420	3.0710	2.880	0.3257	0.9383	0.5819	−1.0850
6	4.0106	0.480	3.3534	3.298	0.2983	0.9819	0.6170	−0.9913
7	4.3752	0.520	3.6634	3.368	0.2730	0.9736	0.5421	−1.055

TABLE 2—LEDEN'S METHOD

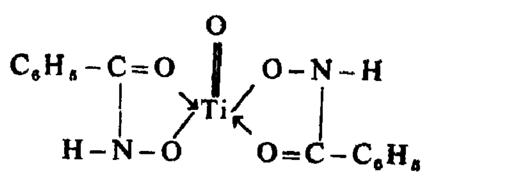
Solution	Total ligand conc. M/lit. ($C_L \times 10^3$)	Absorbance	Equilb. Ligand conc. M/lit. ($L \times 10^3$)	Equilb. Metal conc. M/lit. ($M \times 10^3$)	Conc. of Metal complexed M/lit. ($\times 10^3$)	Degree of complex formation $\phi = \frac{C_M}{M}$	ψ_1 ($\times 10^{-2}$)	ψ_2 ($\times 10^{-4}$)
1	2.9168	0.325	2.4718	1.2355	0.2225	1.180	7.281	1.308
2	3.2814	0.380	2.7612	1.1979	0.2601	1.217	7.859	1.434
3	3.6460	0.420	3.0710	1.1705	0.2875	1.245	7.980	1.329
4	4.0106	0.480	3.3534	1.1294	0.3286	1.291	8.680	1.426
5	4.3752	0.520	3.6634	1.1021	0.3559	1.323	8.816	1 341

Harvey and Manning's method[18], using excess metal for log K_1 and excess reagent for log K_2. The results are given in Table 3.

TABLE 3—STEPWISE STABILITY CONSTANTS FOR TITANIUM COMPLEXES AT 27±2°

Method	log K_1	log K_2	log β_2
Yatsimirskii's	2.23	2.20	4.43
Leden's	1.59	2.54	4.13
Harvey and Manning's	2.25	2.25	4.50

In the normality range of acidity, titanium exists in the form of TiO^{2+} as evidenced from the formula of the isolated complexes[20-22]. Therefore the 1 : 2 complex may be represented by the formula $[TiOR_2]$ where HR stands for BHA. It can also be concluded from the stability data in Table 3 (Yatsimirskii & Harvey-Manning's method) that the ligands acting as bidentate, attack titanium simultaneously and not in a stepwise manner. It may be noted that in a complex with high dissociating tendency, Leden's method is slightly inaccurate, as [M] data are calculated, assuming Beer's Law is obeyed, but in a region where excess ligand is not present. Hence the values for [M] were not exactly correct. Hence, there is discrepancy in the values of log K_1 and log K_2 in Leden's method. The structure of 1 : 2 complex may be depicted as follows :



The 1 : 1 complex, in all probability is [TiORCl]

Microamounts of titanium can be determined at both 4*N* and 8*N* HCl. However, interference from V(V) is more at 8*N* than at 4*N* whereas the reverse is the situation from Mo(VI) and W(VI). Sensitivity and optimum range favour the study at 8*N*.

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Spectrophotometric studies on tributyl tin chloride and butyl tin trichloride with PAN [1-(2-pyridyl azo)-2-Naphthol], Quinalizarin (1-2-5-8—tetrahydroxy anthraquinone, and Alizarin red-S [Sodium salt of (1, 2 dihydroxy-3-anthraquinone) sulphonic acid.

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Tributyl tin chloride and butyl tin trichloride form red, reddish pink and yellowish orange complexes with PAN, Quinalizarin and Alizarin red-S respectively. The complexes with PAN [1-(2-pyridyl azo)-2-Napthol] and Quinalizarin (1-2-5-8 tetrahydroxy anthraquinone) exhibit maximum at 540nm and with Alizarin red-S-(Sodium salt of 1, 2-dihydroxy-3 anthraquinone sulphonic acid), the complexes show the maximum at 475nm.

The composition of the complexes in all the cases is 1 : 1 as determined by Mole Ratio method and Job's Method of continuous variation employing spectrophotometric data.

SPECTROPHOTOMETRIC studies of the chelates of transition metals and rare earth metals in solution have been studied in detail by a large number of workers in recent past[1,2]. The stability constant, structure and the compsoition of the chelates have been determined by using Slope ratio, Mole ratio and Job's method of continuous variation. In the field of organometallic complexes such studies are rare. It may be probably due to the fact that such compounds undergo ready hydrolysis in aqueous solution. It has been observed that certain dyes do yield coloured organotin chelates in solution and their stability constants have been determined spectrophotometrically. Irving and Cox[4] reported the interaction of triphenyl tin chloride with dithiozones and extracted the complexes in carbon tetrachloride. Work on the chelates of organotin compounds with diphenyl carbazones[5] have also been studied colorimetrically. Pilloni[6] has shown by spectrophotometric measurements that the complexes of R_2Sn^{+2} (R = Me, Et, Bu and Ph) with 1-(2-pyridyl azo)-2-Naphthol (PAN) are highly soluble in dioxan and the stability of these complexes decreases in the order of Ph > Bu > Et > Me. Di-ethyl-tin compounds in the concentration range of 2×10^{-6}, 2×10^{-4} *M* are shown to yield 1 : 1 complexes with 4-(2-pyridyl azo) resorcinol (PAR)[7]. It is therefore worthwhile to extend the above investigation in solution and the authors have made a detailed investigation of the following system using 95% ethanol as a solvent.

1. Bu_3SnCl
   ......PAN [1-(2-pyridyl azo)-2-Naphthol]
   $BuSnCl_3$
2. Bu_3SnCl
   ......Quinalizarin (1, 2, 5, 8 tetrahydroxy anthraquinone)
   $BuSnCl_3$
3. Bu_3SnCl
   ......Alizarin Red-S (Sodium salt of 1, 2, dihydroxy 3-anthraquinone sulphonic acid)
   $BuSnCl_3$

Experimental

Doubly distilled ethanol (95%) was used as a medium throughout these investigations and absorbance measurements were made on Beckmann D.B. double beam spectrophotometer using 1 cm matched fused silica cells at a fixed temperature of 35 ± 1°.

All the dyes used in the present investigation form colloidal electrolytic solution and therefore extremely dilute solution in the concentration range of 10^{-5} *M* and 10^{-4} Molar were prepared in doubly distilled ethanol. Stock solutions of 1×10^{-3} *M* concentration of ligands and the Lewis acids were also prepared in the same solvent. For spectrophotometric investigations these solutions were diluted with ethanol and used.

Composition of the Complex :

The composition of the complexes was determined by Mole ratio method[8] and Job's method of continuous variation[9].

(I) ***Mole Ratio Method :***

In this method the spectrophotometric titration

of solution of fixed concentration of ligand PAN, Quinalizarin and Alizarin Red-S with varying amounts of Bu_3SnCl and $BuSnCl_3$ solutions was performed as follows.

Thus a fixed volume (3.0 ml.) of ligands (for PAN $2\times10^{-4}M$, Quinalizarin $.25\times10^{-3}M$ and Alizarin Red-S $1\times10^{-3}M$) were mixed with increasing volumes (0.5 ml. to 6.0 ml.) of the solutions of Lewis acids (e.g. Bu_3Sn^{+1} and $Bu\,Sn^{+3}$ of $2\times10^{-4}M$, $.25\times10^{-3}M$, $1\times10^{-3}M$ solution for PAN, Quinalizarin and Alizarin Red-S respectively). The total volume in all the cases was made up with ethanol to a constant volume (10.0 ml.). The absorbance of these solutions were measured at wavelength of maximum absorption for the complexes. The results are shown in Fig. 1.

(II) *Job's Method of Continuous Variation :*

In Job's method of continuous variation the concentration of both the reactants is varied. All the systems were examined by this method also.

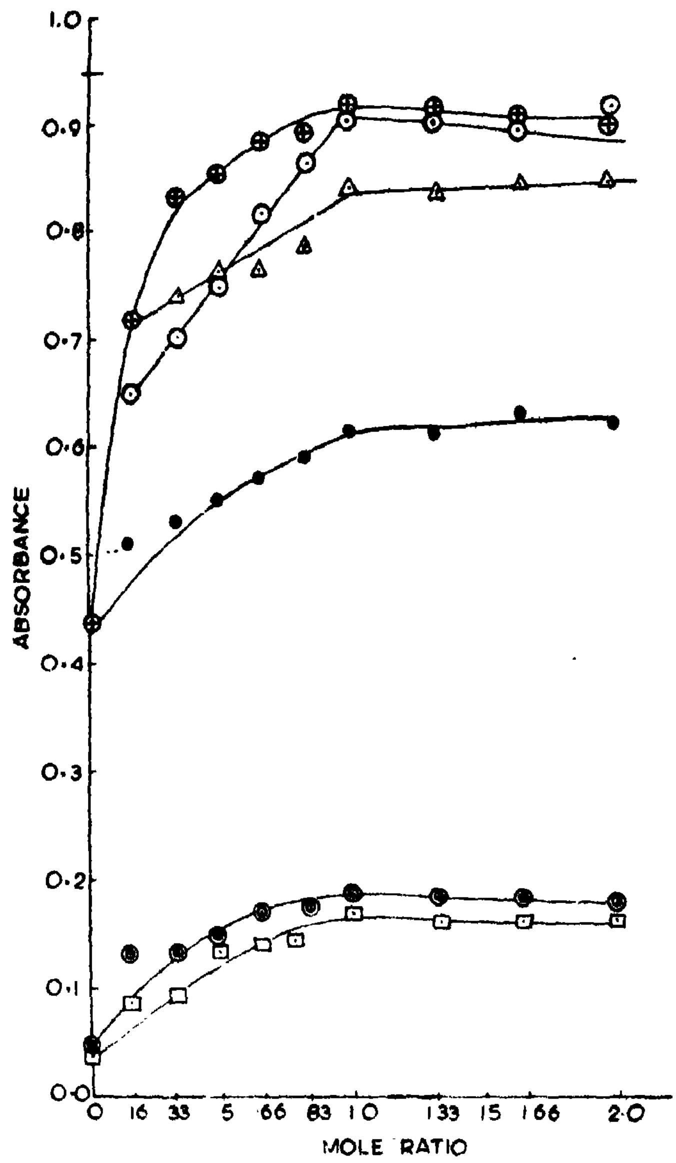


Fig. 1. Spectrophotometric Titration (Mole Ratio Method)
Plot of Lewis Bases against Lewis acids e.g. Tributyl Tin Chloride and Butyl Tin Trichloride

540 nm [□-□ $BuSnCl_3$/PAN; ⊙-⊙ Bu_3SnCl/PAN]

540 nm [⊕-⊕ $BuSnCl_3$/ALIZARIN RED-S; ●-● Bu_3SnCl/ALIZARIN RED-S]

475 nm [△-△ Bu_3SnCl/QUINALIZARIN; ○-○ $BuSnCl_3$/QUINALIZARIN]

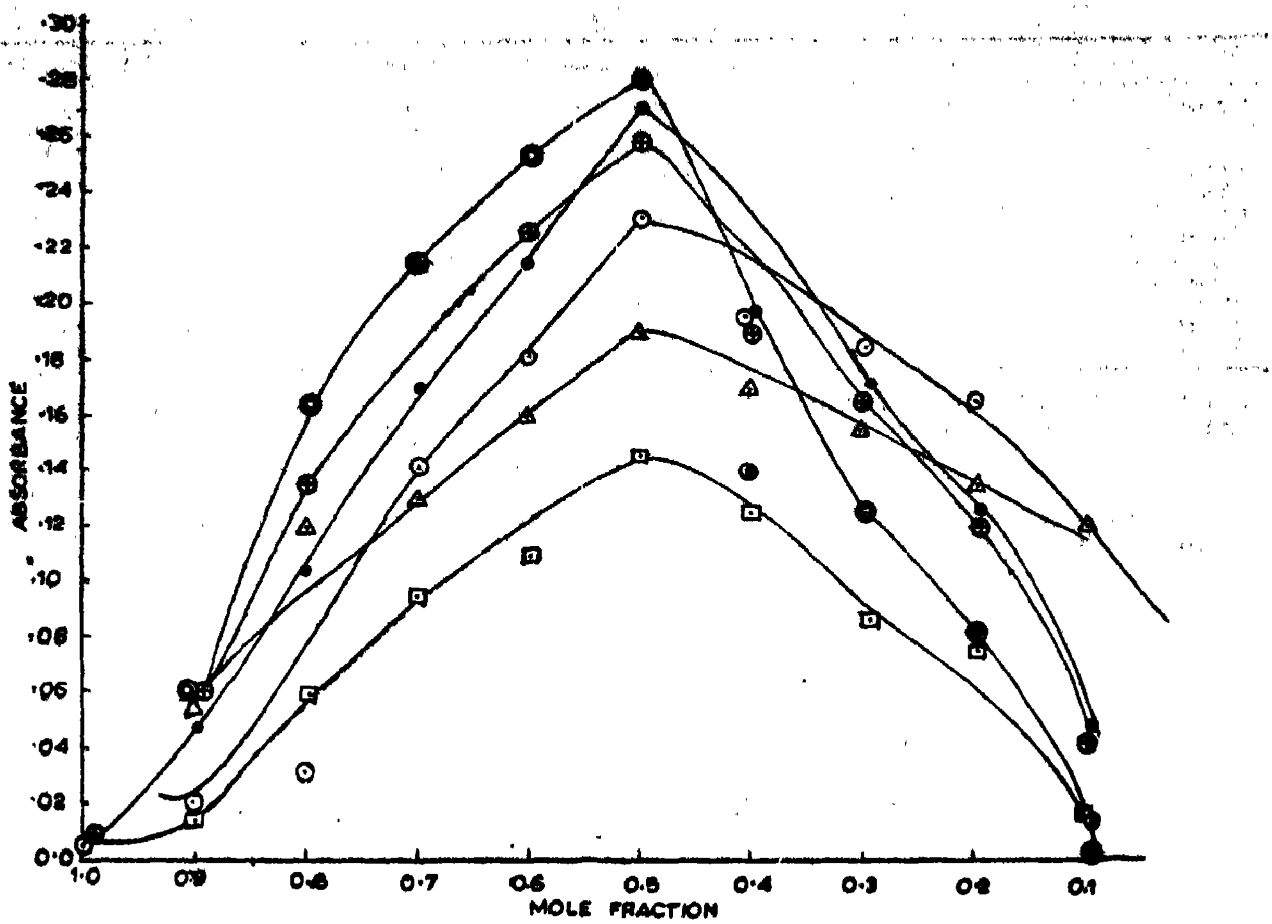


Fig. 2. Job's method of continuous variation. Plot of Lewis bases against Tributyl Tin Chloride and Butyl Tin Trichloride

⊡-⊡—$BuSnCl_3$/PAN ⎤ 540 nm
◎-◎—Bu_3SnCl/PAN ⎦

⊕-⊕—$BuSnCl_3$/ALIZARIN RED-S ⎤ 540 nm
⊖-⊖—Bu_3SnCl/ALIZARIN RED-S ⎦

△-△—Bu_3SnCl/QUINALIZARIN ⎤ 475 nm
○-○—$BuSnCl_3$/QUINALIZARIN ⎦

The stock solutions of Bu_3SnCl & $BuSnCl_3$ and ligand were diluted to $5\times10^{-5}M$ for PAN, $1\times10^{-4}M$ for Quinalizarin and $5\times10^{-4}M$ for Alizarin Red-S complexes. Thus solutions containing varying amounts of Lewis acids $Bu_3\ Sn^{+1}$ & $Bu\ Sn^{+3}$ (0.00 to 10.0 ml.) of requisite concentration were mixed with (10.0 to 0.00 ml.) of equimolecular solutions of ligands. The absorbance of series of solutions so made was measured at the wavelength of maximum absorption. The results are depicted graphically in figure 2.

Colour of the Complex :

When the ethanolic solution of dye is added to the solution of Bu_3Sn^{+1} or $BuSn^{+3}$, the specific changes in colours are summarised in Table-1.

Effect of Time on Colour of the Complex :

The colour was instantaneously produced and there was no change in the absorbance even after 24 hrs. The order of mixing of the reagent also had no effect in the absorbance value.

Effect of Temperature :

Variation of temperature had no effect on colour of the complex. Determinations were made at a temperature $35\pm1°$. Large variation of temp. is expected to effect the results.

Results and Discussion

(a) *System $Bu_3\ Sn\ Cl$, $Bu\ Sn\ Cl_3$/1-(2-pyridyl azo)-2-Naphthol*

The data as collected by the above two methods suggest formation of 1 : 1 complex. The rare possibility of existence of charged complexes in nonaqueous solvents and well established action of PAN[10,11,12] behaving as tridentate ligand leads to the suggestion that in the initial stages the complex mostly exist in the following A-form which is

TABLE 1

Absorption in 95% ethanol for the ligands and their organotin complexes

Ligand	Lewis acid	max nm	max X 10^{-4}	Colour
PAN	X	480	.066	Yellow
PAN	Bu_2Sn^{+2}	540	.31	Red
PAN	$Bu\ Sn^{+3}$	540	.288	Red
Quinalizarin	X	510	.68	Light Violet
Quinalizarin	Bu_2Sn^{+2}	540	1.12	Reddish Pink
Quinalizarin	$Bu\ Sn^{+3}$	540	1.2	Reddish Pink
Alizarin Red-S	X	430	.143	Light Yellow
Alizarin Red-S	Bu_2Sn^{+2}	475	.203	Yellowish Orange
Alizarin Red-S	$Bu\ Sn^{+3}$	475	.303	Yellowish Orange

neutral and it contains hepta-coordinated tin atom with two-five membered rings and this may be in equilibrium with the structure B.

Although it is not certain yet, which of the two structures should be stable and under what condition. Further work in this direction is necessary. Apparently at low *p*H values species A is likely to be more stable while at higher *p*H species B may be expected to be more predominant. Thus there seems to be *p*H dependence in the stability.

FIG. A

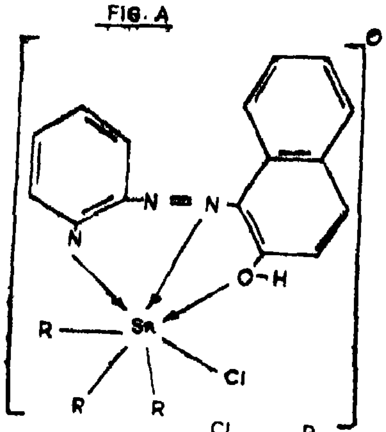
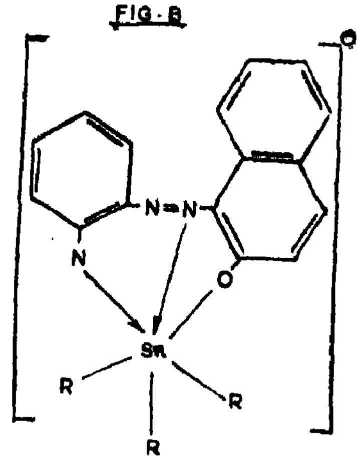


FIG. B



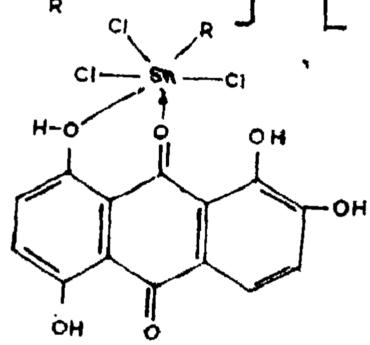


FIG. C

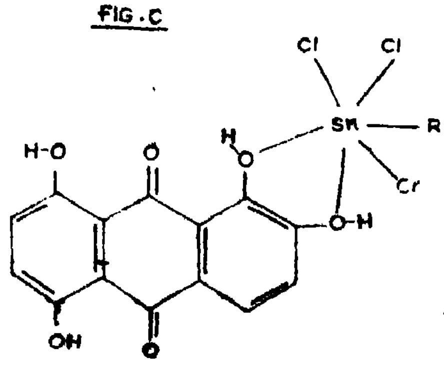


FIG. D

(b) *System Bu_3SnCl, $BuSnCl_3$/Quinalizarin and Alizarin Red-S*

The above data is in confirmity with 1 : 1 complex, it is not possible to suggest unambiguous structures in the above two cases with the help of the collected data. There are two possibilities of chelation.

The chelation can occur from the quinonoid oxygen and the adjacent phenolic oxygen or with the two adjacent phenolic oxygens. The two alternative arrangements are shown by Fig. C and Fig.D resspectively.

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Spectrophotometric Determination of Niobium(V) with Catechol and 1, 2-Diaminocyclohexanetetraacetic Acid

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Niobium(V) reacts with catechol in aqueous solutions in presence of 1, 2-Diaminocyclohexanetetraacetic acid (DCTA) forming an orange red coloured complex with an absorption maximum at 470 nm around pH 3.8 in tartrate medium. The system conforms to Beer's law for an optimum range (for ½" path length) 0.65-9.66 μg/ml of niobium. The behaviour of many cations and anions and also synthetic mixture corresponding to the composition of samarskite mineral were studied for their interference in the determination of niobium.

METHODS for the determination of niobium are generally long and tedious, and require preliminary separation of interfering ions. Masking agents, added to improve selectivity, greatly reduce the sensitivity of many methods. Mixed ligand complexes of niobium and tantalum were studied for their stoichiometry, stability constants[1,2] and analytical determinations[3-6]. Catechol complex of niobium in the presence of DCTA was studied in tartrate medium. Optimum conditions for its analytical determinations were established. Many cations and anions do not interfere in the estimation of niobium and their tolerance limits were also found out and described in this paper.

Experimental

Reagents and equipment : Known weights of specpure (Johnson Mathey and Co) oxides of niobium (0.0266 gm/100 ml) was fused with 1 gm potassium bisulphate and taken in 0.75% tartaric acid.

D.C.T.A. A solution of DCTA (Aldrich Chemical Co) 0.01*M* was prepared in 0.004*M* sodium hydroxide.

Catechol : Freshly prepared aqueous solution of catechol (0.05*M*) recrystallised pure sample (Riedel, W. Germany) was used.

0.75% aqueous solution of tartaric acid (AR), titanium and tantalum in 0.75% of tartaric acid solution (AR) and aqueous solutions of all other foreign ions were used.

A Bausch & Lomb 'Spectronic 20 'Spectrophotometer using 1/2" matched cells and a 'Systronics (India) *p*H meter (Type 322-1) were used.

Procedure

11 ml of catechol, 6 ml of DCTA and varying amounts of niobium in tartrate medium were mixed and the *p*H was adjusted at 3.8±0.1 and made up to 25 ml with distilled water of the same *p*H. The final tartrate concentration was maintained with 1-2 ml of tartaric acid solution including the niobium (tartrate medium) concentration taken. Absorbance measurements can be taken at 470 nm, 8 hours after preparation of the solutions at room temperature (25°).

Results

Niobium(V) in tartrate medium reacts with catechol having no absorption in the visible range but by adding DCTA it forms an orange-red coloured complex with absorption maximum at 470 nm. This colour formation in tartrate medium was utilised for the analytical determination of niobium, after establishing the optimum conditions.

Time and Temperature Study

The formation of niobium complex with catechol and DCTA was slow and completes in 8 hours and remains stable up to 4 days at room temperature. However at higher temperatures the colour intensity decreases probably due to dissociation.

pH Variation

The spectra of the complex in the visible region at different *p*H indicated that absorption maximum at 470 nm persists only in a narrow *p*H region, 3.7 to 4.1. Further work was carried out at *p*H 3.8±0.1.

Effects of Reagent Concentration : Catechol Variation

The effect of catechol variation on colour intensity with 1 ml of metal, 3 ml of DCTA and varying concentrations of catechol solutions at *p*H 3.8±0.1 in total volume of 25 ml indicated that colour saturation was obtained with 11 ml of catechol. Further increase of catechol concentration up to 14 ml indicated no significant change in absorbance values for the above conditions of study.

DCTA Variation

The effect of DCTA on colour formation indicated that colour intensity increases with increasing concentration of DCTA and attains a steady value around 6 ml and remains constant in a region of 5 to 8 ml conc. in total vol. of 25 ml.

Tartaric Acid Variation

For the above system of 1 ml niobium, 6 ml DCTA, 11 ml catechol solutions in 25 ml, the intensity of absorption remained constant in the region of 0.3 ml of tartaric acid in excess of 2 ml of niobium solution in tartrate medium already taken.

Beer's Law Range, Sensitivity

The optimum niobium conc. range for its estimation and measurement at 470 nm using ½" matched cells was found to be 0.65-9.66 μg/ml of niobium and conformity to Beer's law was obtained. Sensitivity of the estimation is 0.013 μg/ml of niobium for A=0.001 absorbance unit and 1.0 cm path length.

Study of Foreign ions

The following foreign ions did not show significant interference in the estimation of 92.96 μg of niobium in 25 ml by the recommended procedure.

W^{6+} (183 μg) ;	Ta^{5+} (92.96 μg) ;	Ti^{4+} (46 μg)
Th^{4+} (2320 μg) ;	Zr^{4+} (730 μg) ;	Cr^{3+} (104 μg)
Al^{3+} (235 μg) ;	Sb^{3+} (121.76 μg) ,	Y^{3+} (689 μg)
Fe^{3+} (111.70 μg) ,	Sn^{2+} (593 μg) ;	Hg^{2+} (4012 μg)
Be^{2+} (92.96 μg) ,	Pb^{2+} (2072 μg) ;	Ca^{2+} (200 μg)
Cu^{2+} (127 μg) ,	Na^+ (4000 μg) ;	K^+ (4000 μg)
NH_4^+ (1000 μg) ;	PO_4^{3-} (2850 μg) ;	SO_4^{2-} (2850 μg)
NO_3^- (2840 μg) ;	Cl^- (2000 μg) ;	

However at lower concentrations Mo^{6+}, F^-, $(COO)^{2-}$ are interfering seriously.

Seven synthetic mixtures corresponding to the composition of Samerskite mineral were estimated with a relative standard deviation of 1%

Nb_2O_5 (44.54%) ;	Ta_2O_5 (8.05%) ;	TiO_2 (1.69%) ;
SiO_2 (0.22%) ;	SnO_2 (1.48%) ;	Fe_2O_3 (14.77%) ;
CaO (0.94%) ;	MgO (0.03%) ;	Al_2O_3 (0.79%) ;
ThO_2 (1.21%) ;	Ce_2O_3 (0.8%) ;	Y_2O_3 (13.93%) ;
MnO (1.60%) ;	PbO (2.04%) ;	UO_2^{2+} (6.08%) ;
Na_2O (0.21%)	K_2O (0.21%) ;	Na_2O(0.29%).

Estimation of niobium by this method will be useful for the analysis of minerals or alloys.

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Determination of Copper and Cadmium Present together in the Binary Mixtures

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This paper reports the results of the determination of copper and cadmium present together in the binary mixtures in low concentrations biamperometrically using two stationary platinum electrodes at constant applied potential of 0.9 volts. The pH at which the determination was carried out was 3.5 for copper and 4.5. for cadmium.

A study of the available literature[1] shows that scarcely attempt has so far been made for the quantitative determination of copper and cadmium present in a mixture by electrometric titrations. Cihalik and others[2] estimated copper and cadmium in a binary mixture using ethanolic mercaptobenzothiazol as a titrant.

The present studies report on the application of biemperometry for a rapid and direct determination of copper and cadmium present in their binary mixtures at low concentration using EDTA as a titrant.

Experimental

Copper and cadmium salts used were of B.D.H. or Merck's extrapure quality. The respective sulphates of copper and cadmium were dissolved separately in conductivity water and their contents estimated using standard methods[3]. Standard EDTA solution (.05*M*) was prepared and standardized using standard methods[3]. Salts solutions were obtained after appropriate dilution of the stock solution. Conductivity water was used for dilution and preparation of solutions.

The apparatus and the experimental arrangements used were same as described in the earlier papers[4]. 20 ml of the test solution containing copper and cadmium was placed in the titration cell with proper amount of monochloroacetate buffer, *p*H 3.5 at an applied potential of 0.9 volts. A stream of nitrogen passed for 5 minutes. EDTA solution was added from a 2.0 ml semimicroburette and the solution was stirred using magnetic stirrer. With the addition of EDTA solution cupric ions chelate the current remains constant till the equivalence point when EDTA completely complexes the cupric ions and thereafter the current begins to increase. Cadmium does not interfere with copper estimation at this *p*H. When the estimation of copper is complete the *p*H of the mixture is altered using acetate buffer and adjusted to 4.6. Next the titration is continued at the same applied potential. Cadmium starts getting chelated with the further addition of EDTA and the current remains steady and increase with the excess of titrant. The graphs obtained by these titrations contain two intersections on the residual current line. The first end point is corresponding to completion of copper determination and the second is corresponding to the sum of copper and cadmium estimation ; the amount of latter is computed by the difference. The curve has the shape as shown in Fig. (1). Experiments were repeated

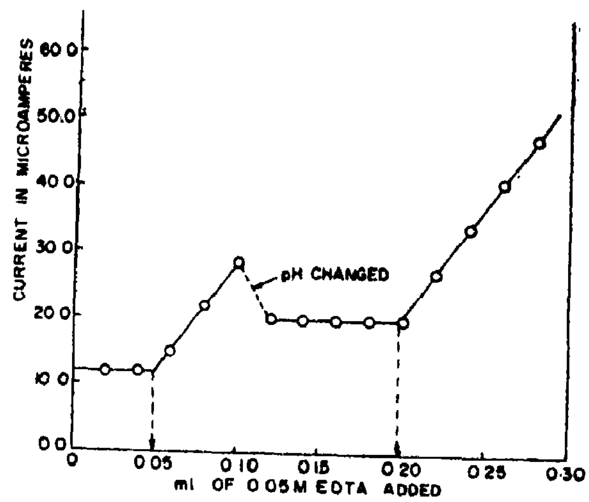


Fig. 1.

Amount observed, mg
Copper Cadmium
0·1913 0·2810

several times for concordance and the results of such determination are given in Table 1.

TABLE—1

DETERMINATION OF COPPER AND CADMIUM PRESENT TOGETHER IN THE BINARY MIXTURES

Amount of cadmium, mg			Amount of copper, mg		
Taken	Found	Difference	Taken	Found	Difference
0.2810	0.2810	±0.0000	0.1906	0.1913	+0.0007
0.2248	0.2259	+0.0011	0.1271	0.1271	±0.0000
0.1967	0.1973	+0.0006	0.1271	0.1277	+0.0006
0.1686	0.1681	−0.0005	0.1191	0.1192	+0.0001
0.1124	0.1115	−0.0009	0.0953	0.0962	+0.0009

Results and Discussion

The method described is based on electro-oxidation of free EDTA on a platinum anode in the *p*H range 3.5 to 4.5 On addition of EDTA solution metal chelates are formed and no electro-oxidation of EDTA occurs. If a potential of the order of 0.9 volts is applied to two platinum electrodes the residual current is registered up to the equivalence point but the current rises abruptly due to the oxidation of EDTA after the equivalence point. The method is sensitive even at low concentrations and the electrode system is both compact and simple ; and would be very useful for the analysis of alloys and minerals. Results are within the limits of experimental errors.

Acknowledgements

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Titrimetric Determination of Chloral Hydrate by Oxidation with Alkaline Potassium Permanganate

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A procedure is described for the volumetric determination of chloral hydrate based on its oxidation at ordinary temperature with alkaline permanganate in the presence of barium ions. Chloral hydrate (40-400 mg) can be determined by the proposed method with a precision of ±0.8% or better.

POTASSIUM dichromate[1], iodine[2,3], bromine[4] and acidic potassium permanganate (in presence of sodium pyrophosphate)[5] have been utilized for the quantitative oxidation of chloral hydrate. Stanciu and Stoicescu[6] heated chloral hydrate with permanganate in presence of sodium carbonate and determined the unused oxidant iodometrically. This method cannot give accurate results because alkaline permanganate undergoes auto-decomposition on heating[7].

In the present communication, alkaline permanganate has been used for the quantitative oxidation of chloral hydrate at room temperature. In strong alkaline solution the reduction of permanganate takes place in two steps. Manganate ion is formed in the first stage which gets further reduced to manganese dioxide in the second[8]. However, in presence of barium chloride, due to poor solubility of barium manganate, the manganate ion concentration is suppressed and hence the decomposition of manganate ion to manganese dioxide is prevented. This fact has been made use of in the proposed method for the determination of chloral hydrate.

Experimental

Sodium oxalate and potassium permanganate used were of A.R. quality. 0.1*M* solution of potassium permanganate was prepared[9] and standardized against sodium oxalate solution[10]. Saturated solution of barium chloride and 10*M* sodium hydroxide solution were prepared from B.D.H. and E. Merck product respectively. Chloral hydrate solution of different concentrations were prepared by dissolving Carnegie Chemicals Limited product in distilled water and standardized with iodine solution.[2]

The oxidation of chloral hydrate with alkaline permanganate is rather slow. Hence, if alkaline permanganate solution is titrated rapidly with a solution of chloral hydrate, the reaction is incomplete and so more volume of chloral hydrate is required than calculated theoretically. On doing the titration too slowly the auto-decomposition of permanganate occurs considerably and the titre value obtained is less than the stoichiometric value. This difficulty has been obviated in the following manner.

Procedure

25 ml of 0.1*M* potassium permanganate and 10 ml each of 10 *M* sodium hydroxide and saturated barium chloride solutions are taken in an Erlenmeyer flask. The mixture is heated to about 80° and titrated (in 2-3 minutes) with the solution of chloral hydrate to be determined. The approximate titre so obtained is noted. The same reaction mixture is again taken, the volume of chloral hydrate corresponding to approximate titre is at once added and it is stirred for about 5 minutes. Chloral hydrate solution is very slowly added through a microburette with constant stirring till the pink colour disappears. The rate of addition of titre is so adjusted that about 15 minutes are required for the completion of titration.

1 ml of 0.1*M* potassium permanganate ≡ 8.271 mg of chloral hydrate.

The results for the evaluation of chloral hydrate solution of different concentrations have been recorded in Table-1.

TABLE—1

Expt. No.	Chloral hydrate used for titration (M)	Amount of chloral hydrate on base of 2 electron change (mg)		% Error
		Theoretical	Obtained	
1.	2.0000	413.550	410.241	−0.8
2.	0.2000	206.775	206.750	0.0
3.	0.0500	82.710	83.871	+0.8
4.	0.0125	41.355	41.670	+0.7

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Studies on the Use of Acetothioacetanilide as a Reagent for the Gravimetric Determination of Nickel(II) and Cobalt(II)

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Nickel(II) and cobalt(II) have been precipitated from solutions of pH 6.4-6.9 and 6.7-12.0 as their acetothioacetanilide complexes of formulae $Ni(C_{10}H_{10}ONS)_2$ and $[Co(C_{10}H_{10}ONS)_2]$ which can be weighed after drying at 110° and 80° respectively. The relative standard deviations are ±0.46% and ±0.45%. The composition of the complexes have been studied by elemental analysis, thermogravimetric studies and magnetic measurements, Separation from several diverse ions, including Fe^{3+}, Al^{3+}, Cr^{3+}, Mn^{2+}, VO^{2+}, AsO_4^{3-} and MoO_4^{2-} have been effected using tartrate or sulphosalicylic acid as masking agent. Nickel content of a few samples of stainless steel has been determined using ion-exchangers for preliminary separations as masking of the foreign ions was not possible when they were present in large excess.

ALTHOUGH the most common reagent for the gravimetric determination of nickel is dimethylglyoxime[1], various thiocompounds[2-5], have been used for the same purpose. Several thiocompounds[6-9] have also been recommended for the gravimetric estimation of cobalt.

The object of this investigation is to study the applicability of the ligands capable of forming chelates through one oxygen and one sulphur atom for the determination of nickel(II) and cobalt(II). A new reagent, acetothioacetanilide, $CH_3.CO.CH_2.CS.NH.C_6H_5$ has been found to give weighable complexes with both.

Experimental

Acetothioacetanilide solution : The reagent was prepared following the method due to Barnikow, Kunzek and Richter[10]. Fresh solutions of the reagent were prepared by dissolving 0.20 to 0.35g of it in minimum volume of 2*N* aqueous ammonia.

Nickel(II) solution : Pure nickel chloride (G.R., E. Merck) was dissolved in very dilute hydrochloric acid and the metal content was determined gravimetrically using dimethylglyoxime[1].

Cobalt(II) solution : A stock solution of cobalt(II) sulphate (A.R., B.D.H.) was prepared and cobalt was estimated with α-nitroso-β-naphthol[11].

All the other chemicals were of analytical grade.

Apparatus : A Cambridge bench model *p*H-meter was used to control the *p*H-values and the magnetic measurements were carried out in a standard Guoy balance. The thermogravimetric studies were carried out with a Photorecording Metriplex Derivatigraph OD-102 (Hungary).

Procedure for nickel(II) : An aliquot of the nickel solution containing 8 to 20 mg of nickel was diluted to about 125 ml with water, mixed with 2g of ammonium chloride, the *p*H was adjusted to 2-3, and heated to 45-55°. The reagent solution was added and the *p*H was raised to 6.4-6.9 with aqueous ammonia (2*N*) to precipitate the brown complex. After 15 minutes, the complex was filtered through a sintered glass crucible (No. 4) and washed with warm (50°) water adjusted to *p*H 6.5. The precipitate was dried at 100-110° and weighed as $Ni(C_{10}H_{10}ONS)_2$ containing 13.25% of the metal. The results are presented in Table 1.

TABLE 1—DETERMINATION OF NICKEL OR COBALT

Metal ion	Weight taken (mg)	Wt. of complex (mg)	Metal ion found (mg)	Rel. error (%)
	8.62	66.00 ; 65.70	8.75 ; 8.71	+1.52 , +1.08
Ni^{2+}	14.37	108.30 , 109.20	14.35 ; 14.47	−0.10 ; +0.73
	20.11	150.95 · 152.55	20.02 ; 20.23	−0.45 , +0.59
	7.68	82.83 ; 82.79	7.67 ; 7.66	−0.23 , −0.28
Co^{2+}	9.60	103.20 , 103.30	9.55 , 9.56	−0.53 ; −0.44
	13.44	144.80 ; 144.50	13.40 , 13.38	−0.30 , −0.44

Nickel was also determined in several samples of steel (Table 2) after preliminary separations using ion-exchangers[12].

TABLE 2—DETERMINATION OF NICKEL IN STAINLESS STEEL

Composition, (%)	Ni found, (%)	Rel. error, (%)
Ni, 9.48 ; C, 0.10 , Cr, 17.51	9.52 ; 9.48	+0.42 ; Nil
Ni, 13.43 ; C, 0.06 ; Cr, 16.47 Mo, 2.70	13.62 , 13.56	+1.49 ; +0.97

Procedure for cobalt(II) : A known quantity of

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the stock solution containing 6-13 mg of cobalt(II) was mixed with 1 – 1.5g of ammonium chloride, diluted to 125ml and the pH was adjusted to 3-4. The mixture was heated (45-50°) and the reagent solution was added. The pH was raised to 6.7 – 12.0 with aqueous ammonia. A green precipitate was formed immediately which was left on water-bath for 15 mins at 45-50° before filtration. The complex was washed with warm (40-45°) water of pH 7.0 and weighed after drying at 80° for 90 mins. The cobalt content was calculated using a factor 0.0926. The results are given in Table 1.

The proper masking agent was added before the addition of the reagent when separation of nickel or cobalt from diverse ions were effected.

Results and Discussion

Properties and composition of the complexes : The nickel complex was brown-grey in colour, while the cobalt complex was green. Both the complexes were soluble in common organic solvents. An ethanolic solution of the reagent could also be used provided the final concentration of ethanol did not exceed 5%.

Both the complexes were dried and analysed for nitrogen by Kjeldahls (micro) method and also for the metal content[1,11] after decomposing the complexes. The experimental results, Ni(Calc. 13.25%, found 13.16, 13.23%), N(Calc. 6.32%, found 6.22, 6.35%) and Co(Calc. 9.26%, found 9.29, 9.27%), N(Calc. 6.60%, found 6.60, 6.62%) indicated the formulae to be

$$Ni(C_{10}H_{10}ONS)_2 \text{ and } H[Co(C_{10}H_{10}ONS)_3].$$

Magnetic Data and thermal decomposition studies : The nickel(II)-bis-acetothioacetanilide chelate was found to be diamagnetic indicating a square planar arrangement. The cobalt(II) complex on the other hand was paramagnetic (μ, 2.98 B.M.), corresponding to octahedral configuration.

Both the complexes were mixed with appropriate quantities of aluminium oxide and subjected to thermogravimetric studies. The nickel complex was stable upto 180° whereas that of cobalt started decomposing at 85°.

Effect of pH and concentration of the reagent : The pH ranges for quantitative precipitation were 6.4-6.9 for nickel and 6.7-12.0 for cobalt. For the former, at least three times the reagent theoretically calculated, were required, while the same for cobalt was three and half times.

Effect of sequestering agents : The determination of nickel or cobalt was possible in the presence of fluoride or sulphosalicylate. Phosphate and tartrate had no adverse effect in the precipitation of nickel though masked cobalt partially. Nitrilotriacetate, ethylenediamine tetraacetate, cyanide, ethylenediamine, citrate or thioglycolate, prevented the precipitation of both nickel and cobalt.

Effect of diverse ions : The presence of arsenate or molybdate did not interfere with the estimation of nickel or cobalt. Sulphosalicylic acid was used to mask iron (III), manganese (II) and vanadyl ions in case of both cobalt and nickel as well as for the separation of nickel from chromium or cobalt from aluminium. Sodium potassium tartrate was used to mask iron(III), chromium(III), manganese(II), bismuth(III), tin(II), antimony(III) or molybdenum(IV) in the determination of nickel. The results of these separations are given in Table 3.

TABLE 3—SEPARATION OF NICKEL AND COBALT FROM DIVERSE IONS

Metal ion (mg)	Diverse ion (mg)	Masked by	Metal ion found (mg)	Rel. error (%)
	Fe^{3+} ; 20	a	14.22 ; 14.29	−1.03 ; −0.52
	Fe^{3+} ; 30	b	14.29 ; 14.35	−0.52 ; −0.10
	Cr^{3+} ; 15	a	14.31 ; 14.32	−0.38 ; −0.31
	Cr^{3+} ; 15	b	14.37 ; 14.39	nil ; +0.14
	Mn^{2+} ; 30	a	14.23 ; 14.22	−0.94 ; −1.01
Ni^{2+}, 14.37	Mn^{2+} ; 15	b	14.26 ; 14.29	−0.73 ; −0.52
	Sn^{2+} ; 30	a	14.25 , 14.32	−0.80 ; −0.31
	Sb^{3+} ; 30	a	14.29 ; 14.31	−0.52 ; −0.38
	Bi^{3+} ; 30	a	14.35 ; 14.37	−0.10 ; nil
	MoO^{2+} ; 15	a	14.32 ; 14.37	−0.31 ; nil
	VO^{2+} , 10	b	14.22 ; 14.25	−1.01 ; −0.80
	AsO_4^{3-} ; 30	—	14.39 ; 14.37	+0.14 ; nil
	MoO_4^{2-} ; 15	—	14.21 ; 14.29	−1.08 ; −0.52
	Al^{3+} ; 30	b	9.52 , 9.55	−0.85 , −0.53
	Fe^{3+} ; 5	b	9.54 ; 9.48	−0.64 ; −1 21
Co^{2+}, 9.60	Mn^{2+} , 10	b	9.51 ; 9.57	−0.92 ; −0.32
	VO^{2+} ; 10	b	9.57 , 9.59	−0.32 ; −0.12
	AsO_4^{3-} ; 30	—	9.58 , 9.58	−0.26 ; −0.26
	MoO_4^{2-} , 60	—	9.54 , 9.57	−0.64 ; −0.32

(a) tartrate , (b) sulphosalicylate.

However the relative error was too high (>1%) when iron or chromium was present in large excess. For such mixtures, e. g. in case of stainless steel, preliminary separation using ion-exchangers was necessary.

Standard deviation : The relative standard deviation for 30 determinations for each of the metals were ±0.46% for nickel and ±0.45% for cobalt.

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Studies on the Changes in DTPA-extractable Micronutrients (Fe, Mn & Cu) in Soils following Incubation and Plant Uptake

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The DTPA-extractable iron, manganese and copper status of three alluvial soils and their change in amount on equilibriation for a period of seven days at moisture-saturation and subsequently after growing soybean plants on those soils for a period of one month have been studied. The amount of iron, manganese and copper was increased in all the three soils after seven days of incubation from which it can be concluded that the mobilization of the micronutrients in soils was increased on incubation under moisture-saturated condition. After growing crop for a period of one month under similar conditions amount of the micronutrients again came down almost to the original levels. The apparent decrease in availability of those micronutrient elements is obviously due to plant uptake and partially due to microbial consumption and refixation in soil.

THE role of micronutrients in plant nutrition has become firmly established both in agricultural sciences and in broad-scale agricultural practices. Although most arable soils are well supplied with micronutrients the problem of deficiency has cropped up with the intensive cultivation and various chemical fertilizers such as phosphate application practices followed in recent years. Besides, it is not the total amount but the available quantity of any micronutrient which is important in deciding the actual uptake by a particular plant under any particular soil condition. As the ultimate source of micronutrients is the soil, it is necessary to know the available micronutrient status of a soil. Among the various methods employed for the determination of available status of micronutrients like copper, iron and manganese, the DTPA (Diethylene triamine penta acetic acid)-extraction developed by Lindsay & Norvell[1] has been found to best correlate with the plant uptake. Although Lopez and Graham[2] later used a modified DTPA-extractant to determine the labile pool of Zn, Fe, Mn and Cu in soil at different *p*H values, the former method is still considered to be extremely useful for monitoring the availability of those cations in soil.

In the present investigation, the changes in DTPA-extractable micronutrients (Fe, Mn, & Cu) in three alluvial soils on incubation for one week under moisture saturated condition have been studied. Changes in available micronutrient status of the same soils, after growing soybean plants on them for a period of one month, have also been investigated.

Experimental :

Three soils used in the present investigation were obtained from the State Livestock Farm, Kalyani (K-soil), the Viswa Vidyalaya Teaching Farm, Mandowri (M-soil) and from the village of Chakdah (C-soil) respectively—all belonging to the district of Nadia, West Bengal. The fields from which the upper 23 cm layer of the soils were collected are under the programme of intensive cultivation. All the soils are light, medium-textured and belong to the comparatively recent Gangetic alluvium which show no sharp profile development. The soils were air-dried, ground and sieved through a 0.2 mm sieve. Some physico-chemical properties of the soils necessary for an understanding of the results of the present experiment are shown in Table 1.

TABLE—1

PHYSICO-CHEMICAL PROPERTIES OF THE SOIL SAMPLES.

Sl. No. of Expt.	Property	Results of analysis		
		K-soil	C-soil	M-soil
1.	Saturation Percentage (%)	5.6	4.4	4.8
2.	Soil *p*H (1 : 2.5 soil water ratio)	8.2	8.4	7.7
3.	Available P_2O_5 (ppm)	40.0	24.5	13.0
4.	Nitrogen (%)	0.09	0.08	0.06
5.	Organic Carbon (%)	0.64	0.61	0.45
6.	C : N ratio	7.21 : 1	8.08 : 1	7.65 : 1
7.	CEC (me/100 gm)	44.0	31.7	18.5
8.	Total Free oxides of Iron (Fe_2O_3%)	0.95	1.51	1.35

Procedure : 800 gms of each soil were taken in plastic pots which were coated externally with coal-tar and the soil inside was maintained at moisture-saturated condition by applying appropriate amount of de-ionized water. The pots including three replications for each soil sample, were kept at room temperature and after seven days of incubation 10.0 gms of soil were sampled out from each pot with the help of a spoon-headed spatula for subsequent extraction of the micronutrient elements. Afterwards, in each pot five seeds of soybean *(Glycine max* Merr.*)* were sown and the

moisture status of the soils in the pots were maintained at saturated condition as before by adding requisite quantity of water. The seeds were previously germinated in a growth chamber and washed thoroughly with de-ionized water. A control series with the usual replications were also simultaneously run.

After one month the plants were taken away from the pots, roots were carefully eliminated and the contents of the pot were thoroughly mixed. Subsequently, 10.0 gms of this soil (on dry-weight basis) were taken and analyzed for DTPA-extractable iron, manganese and copper.

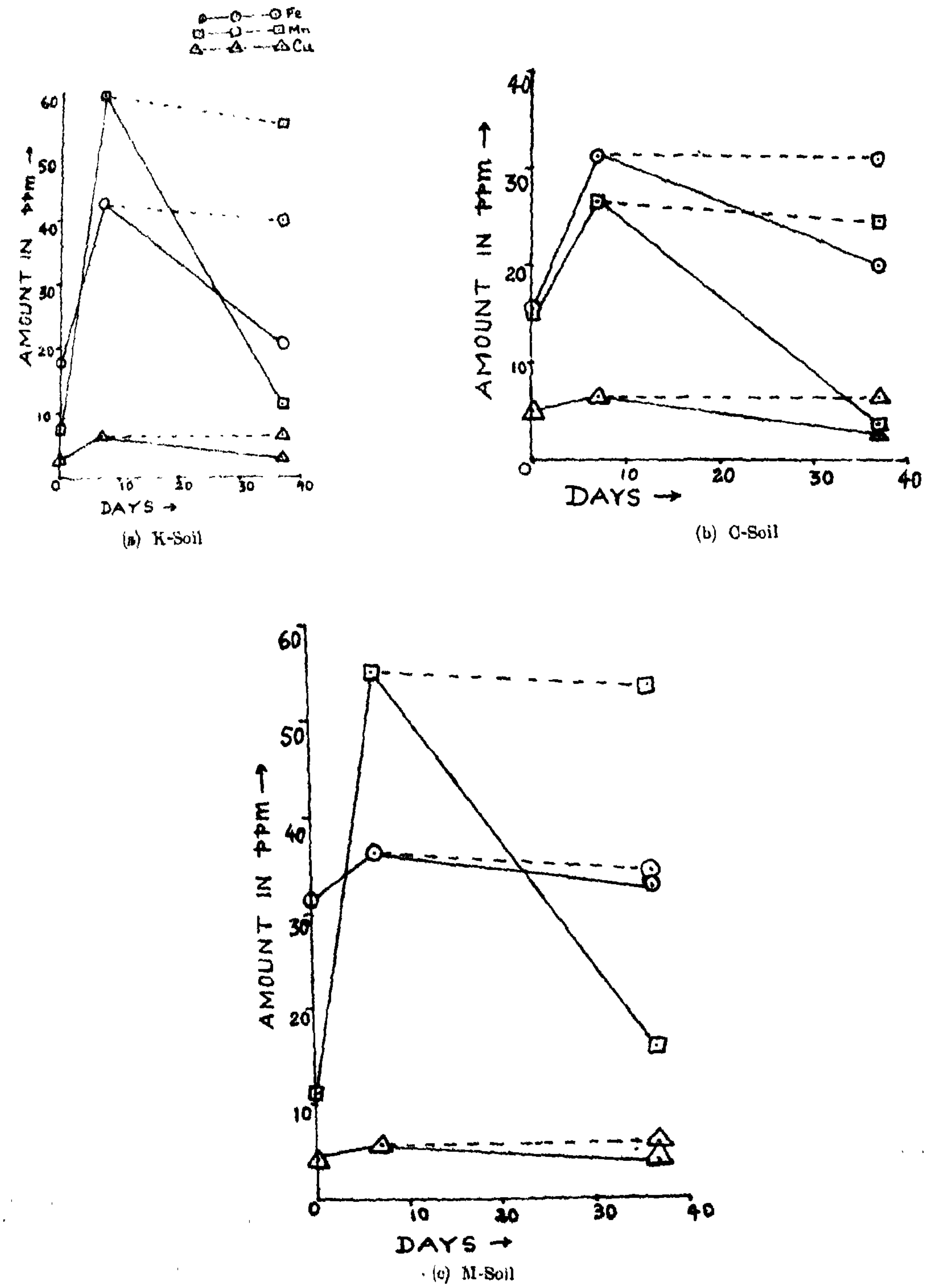


Fig. 1 (a, b, c) Changes in DTPA-Extractable Fe, Mn & Cu in Soil on Incubation.

Extraction : The soil (10.0 gms) was shaken with 20 ml of the DTPA-extractant solution for 2 hours and filtered. The DTPA-triethanolamine extractant was prepared in the same manner as proposed by Lindsay and Norvell[1]. To the filtrate 3 ml of concentrated nitric acid and 5 ml of concentrated sulphuric acid were added and the resulting solution was digested on a hot plate. The digestion procedure was repeated with another 2 ml of concentrated nitric acid until all the organic matter and the metal-DTPA chelates were completely decomposed. The resulting material was taken with redistilled water and the volume was made upto the mark in a 50 ml volumetric flask. Appropriate aliquots were taken from this solution for the estimation of iron, manganese and copper by the usual colorimetric methods as outlined below.

Estimation of iron : Iron has been determined by reduction of ferric iron to the ferrous state with hydroxylamine hydrochloride and subsequent formation of an intense red ferrous chelate with orthophenanthroline as described by Snell and Snell[3] and also cited by Jackson[4].

Estimation of manganese : Manganese was estimated colorimetrically by the periodate method developed by Willard and Greathouse[5]. It is based upon the oxidation of all manganese species at lower oxidation states to MnO_4^- by potassium metaperiodate in a strongly acid solution.

Estimation of Copper : Copper was estimated colorimetrically by the method of Cheng and Bray[6]. In this method a mixture of citrate and EDTA was used as masking agents for most of the interfering ions without preventing formation of the complex between copper and diethyldithiocarbamate. The Copper-complex was extracted by redistilled carbon tetrachloride and then measured colorimetrically.

A Spectronic-20 (Bausch & Lomb) spectrophotometer was used for all absorbance measurements.

All the reagents and chemicals used were of A.R. quality.

Results and Discussion

The analytical data for DTPA-extractable micronutrients under present investigation are given in Table 2. The table contains the values for both air-dried original soil samples and the incubated ones.

It is evident from the results that the amount of DTPA-extractable iron increased in all the three soils after seven days of incubation under moisture-saturated condition. The values decreased nearly to the original level after growing soybean plants on those soils for a period of one month.

The DTPA-extractable manganese content of all the soils were found to increase considerably on incubation, but after growing soybean for one month the corresponding amounts were found to be greater than the original ones in both K-soil and M-soil. In case of C-soil however, the DTPA-extractable manganese was decreased to a level much lower than that of the original values.

A slight increase in DTPA-extractable copper was found in all the three soils after seven days of incubation. After growing the crop for one month on those soils it was reduced to much lower values in case of C-soil and M-soil but almost to the same values in K-soil.

The changes in DTPA-extractable iron, manganese and copper are also shown graphically in Figs. 1. (a, b, c). From Table 2 and from the figures it is clear that there is increase in mobilization of all the three micronutrients in soil on incubation under moisture-saturated condition. Venkata Subrahmanyam and Mehta[7] also observed that availabilities of iron and manganese in soil increase considerably under such a condition. On prolonged incubation, however, no further increase in available status of the above micronutrients was obtained. On the contrary, a slight decreasing trend was

TABLE—2

CHANGES IN THE AMOUNT OF DTPA-EXTRACTABLE Fe, Mn AND Cu

	K-Soil			C-Soil			M-Soil		
	Air-Dry Soil	After 7 days of incubation	After one month of crop grown	Air-Dry Soil	After 7 days of incubation	After one month of crop grown	Air-Dry Soil	After 7 days of incubation	After one month of crop grown
Fe (ppm)*	18.13	42.50	20.63 (39.65)**	15.63	31.25	20.00 (30.80)	31.25	36.25	32.50 (36.04)
Mn (ppm)*	7.50	59.38	11.25 (54.50)	15.02	26.75	3.75 (24.65)	11.25	55.00	15.63 (53.85)
Cu (ppm)*	2.75	6.50	2.88 (6.40)	5.02	6.50	2.50 (6.42)	4.25	5.75	3.88 (5.70)

* The values given are mean of three replications.

** Figures in parenthesis denote the corresponding values of the control.

noticed in all cases as is indicated by the dotted portion of the curves in the figures. This is obviously due to any possible microbial consumption and refixation of the elements in soil.

As regards rate of mobilization, among the three soils K-soil seems to be more susceptible to moisture treatment. On incubation under moisture-saturated condition the K-soil shows about a 2.5-fold increase in available iron and 7.5-fold increase in available manganese. The rate of increase of available copper is also highest in this soil in comparison with the other two soils. The reason for this higher rate of microcutrient mobilization in the K-soil may be attributed to the higher organic matter content and the resulting instant lowering of *p*H or more intense reducing environment set up under such circumstances. That lowering of *p*H through the influence of adequate moisture causes an increase in availability of a micronutrient like manganese is also evident from the observation of Hossner and Blanchar[8].

On growing plants for a period of one month a slight overall increase in DTPA-extractable micronutrient elements is expected in all the three soils, obviously due to mobilization of those elements from the so-called non-labile or semi-labile pool through the influence of root interception whereby some organic chelating agents are produced which tend to hold more micronutrients in solution. An apparent decrease in the amount of available micronutrients in soil after growing plants on them is supposed to be mainly due to plant uptake or crop removal as well as in part, due to fixation in soil in course of prolonged incubation. In case of K-soil the decrease in available micronutrient status is quite conspicuous. Narrower C : N ratio coupled with high available P_2O_5-content of the K-soil may be responsible for the above decrease in available micronutrient status through microbial consumption or chemical fixation.

Further studies on the actual plant uptake of the micronutrients during various stages of the growth period involving plant tissue or dry matter analysis are in progress.

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Effect of Tumour Development on Glucose-6-phosphate dehydrogenase of Host's Liver

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Liver glucose-6-phosphate dehydrogenase activity of Ehrlich ascites carcinoma bearing mice and of mice with skin carcinoma was found to be increased with the development of the tumour. Administration of mitomycin C and refampicin reveals a definite tumour-host relationship as regards the liver glucose-6-phosphate dehydrogenase activity.

GLUCOSE-6-phosphate dehydrogenase (G-6-PD) activity was reported to be increased in hepatomas and other tumours[1-5]. It was, therefore, considered worthwhile to study the behaviour of this enzyme in liver during carcinogenesis in mice bearing fast-growing Ehrlich ascites tumour and slow growing methyl cholanthrene induced carcinoma. The present paper provides information as to this assessment and liver G-6-PD activity has been found to be proportional to the growth of these two types of tumours.

Experimental

Ehrlich ascites carcinoma (EAC) was maintained in Swiss male mice weighing 15-20 gms by inter-peritoneal inoculation of 0.2 ml of ascitic fluid. Iliac region of Swiss male mice of 18-20 gms in average weight were shaved 24 hrs before the first painting and a single brush stroke of 20-Methyl-cholanthrene (0.5% solution in benzene) was applied to that area thrice in a week, over a period of 14 weeks. Another set of mice with benzene painting was kept as control.

Liver was homogenized in 0.25 *M* sucrose solution. Supernatant fraction, after centrifugation at 105,000 g for hr was used for assay. The enzyme was assayed spectrophotometrically[6] by following increase of optical density at 340 nm. Specific activity was expressed as μ moles of TPN^+ reduced/mg protein/min. Protein was determined by the method of Lowry *et al*[7].

Mitomycin C (4 mg/kg b.w.) and Rifampicin (100 μg/ kg b.w.) were injected interperitoneally in EAC-bearing mice. The serial injection (one injection per day) was started 30 mins after transplantation of the tumour and was continued till 10th day. The animals were sacrificed 24 hrs after each injection. Peritoneal fluid of the transplanted animal was taken out in a centrifuge tube. The cells were washed repeatedly with 0.85% saline and the packed cell volume (ml) was determined after centrifugation at 3000 g for 10 minutes.

Results

It can be seen from Fig 1, that the G-6-PD activity in liver increases significantly with the development of the tumour. Within 4th day after transplantation, when the tumour was not even perceptible, the enzyme activity increased by about 40% above the enzyme activity of the normal liver. The increase was very rapid between 2nd and 4th day and was about 79% on 10th day.

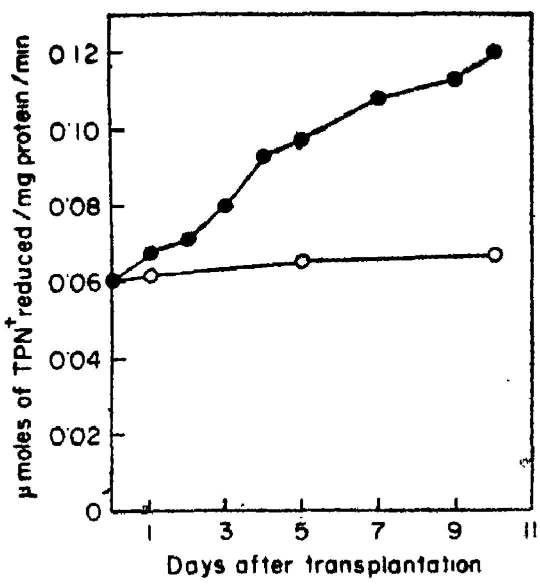


Fig 1. Liver G-6-PD activity of Ehrlich ascites carcinoma-bearing mice.
(○—○) normal liver ;
(●—●) liver of EAC-bearing mice.

In case of slow-growing induced carcinoma, liver G-6-PD showed 27% increase in activity over that of the control liver after one month (Table 1). Incidentally, papilloma was not found at all during this period. Consequently, with the development of carcinoma, activity increased to about 60% on 3rd month. The results showed that during the course of epidermal carcinogenesis, the enzyme activity in

liver increased and reached a higher level than that found in the liver of benzene-painted mice.

TABLE 1.

Liver G-6-PD activity in 20-methylcholanthrene treated mice.

Days of treatment	Weight of the liver (mg)	Sp. Activity (μ moles of TPN^+ reduced/ mg protein/minutes)
	Liver of Benzene painted mice.	
30	800	0.04
60	900	0.014
90	900	0.052
	Liver of 20-methylcholanthrene painted mice	
30	800	0.051
60	700	0.075
90	600	0.083

Values are an average of three experiments.

Hence, some antitumour agents were used to study their effect on tumour growth as well as on the enzyme activity. It can be observed from Table 2 that the administration of mitomycin-C to the transplanted mice caused a regression of ascites tumour without any change in enzyme activity in liver. With rifampicin, however, the liver enzyme activity increased progressively along with the growth of the tumour.

TABLE 2

Effects of Mitomycin C and Rifampicin on EAC-bearing mice.

	Days after transplantation.	Packed cell vol. (ml)	Specific activity of liver (G-6-PD) (μ moles of TPN^+ reduced/mg protein/min).
	1	0.2	0.06
	3	0.2	0.061
Mitomycin C	5	0 1	0.064
	7	0 02	0 064
	9	Nil	0.06
	11	Nil	0 06
	1	0.1	0.06
Rifampicin	3	0.3	0.072
	5	0.1	0 08
	7	0.5	0.088
	9	1.0	0.09
	11	1 3	0 13

Each value represents the average of three experiments.

Discussion

We selected fast-growing Ehrlich ascites tumour and slow-growing methylcholanthrene-induced carcinoma for our study because the definite change in enzyme activity in both cases will show how tumour growth affects the enzyme activity of the host's liver. The data obtained under these two conditions, show a definite increase in G-6-PD activity in host's liver when tumours were still very small. The increased level of activity was very significant when the tumour attains its maximum size. The packed cell volume can be taken as a measure of the growth of Ehrlich ascites tumour. The increase in enzyme activity in liver of benzene-painted animal may be due to some toxic effect. But this increase in activity is much less in comparison to that of the methylcholanthrene painted mice.

Experiments with rifampicin and mitomycin-C show the effect of tumour growth on the level of enzyme activity in liver. The reason for rifampicin not having any inhibitory effect on the growth of tumour could be due to the fact that rifampicin is not very much effective in eukaryotic cells. It can thus be concluded that the tumour development has definite correlation with liver G-6-PD activity, which is quite significant from the early stage of malignancy.

Acknowledgements

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NOTES

Radiochemical and Thermal Studies of the Copper(II)-Exchanged Form of Synthetic Zeolite Linde Sieve A

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Synthetic zeolite Linde Sieve A displays a double ion-sieve action. Only small cations can penetrate the single 6-rings into the beta cages. Ion exchange equilibria in Zeolite A have involved mostly univalent and divalent counterions[1]. The radiochemical and thermal studies of a few cation-exchanged forms of the zeolite have already been reported[2,3]. The present study of copper(II)-exchanged form of 4A shows evidence of hydrated copper(II) ions in the zeolite structure.

Experimental

The bulk supply of the synthetic zeolite used for cation-exchange with copper(II) was from the Union Carbide International Company, U. S. A. and had a lot number 440522. The sample of the zeolite, obtained from the bulk, and its copper(II)-exchanged form were prepared by the method reported by earlier workers[4]. AnalaR quality of copper(II) chloride was used for cation exchange. The exchanged form of the zeolite was washed thoroughly to remove all free copper(II) ions. The washings were treated with ammonia solution for this purpose. The copper zeolite was irradiated for 5 minutes in a neutron flux of 1.3×10^{12} neutrons/cm^2/sec. to get copper-64 by neutron, gamma reaction. The gamma spectrum of the radioactive sample confirmed the presence of copper-64. The copper-64 content was measured in the zeolite against the standard copper(II) chloride which was simultaneously irradiated under similar conditions. The detectors used were Nuclear Enterprise 8312 Automatic Beta Gamma Spectro-

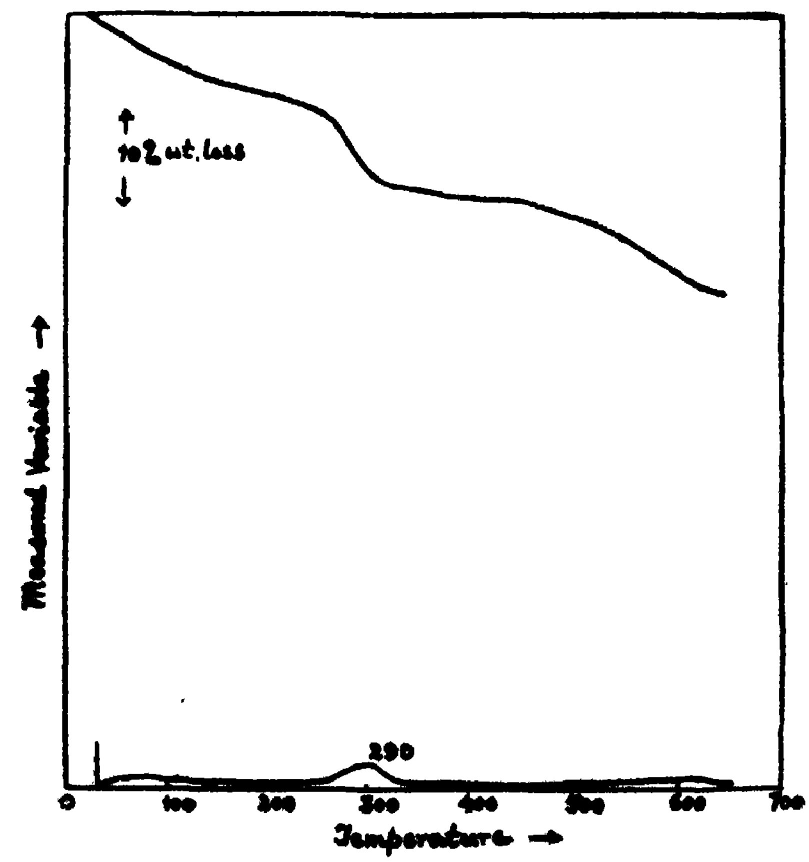


Fig. 1 : TGA of Copper zeolite

meter and Princeton Gamma-Tech. Ge(Li) Detector (Model LGC 4.5 SD) using data presentation units like model 291 for memory, model 292 for display and model 293 for control. The zeolite was found to contain about 40% copper which was far greater than that expected in a completely exchanged Cu_6A zeolite ($A = Al_{12}Si_{12}O_{48}^{12-}$). The copper zeolite was heated to 110° and 650° and these preheated samples were treated with a saturated solution of NH_4Cl aq. The radiochemical analyses of these samples showed about 33% and 10% exchange respectively with NH_4^+ ions.

The thermal studies of the copper zeolite were carried out on a Dupont 990 Series unit for DSC and TGA, under nitrogen and at a heating rate of 20°/minute. The curves are reproduced in Figs. 1 and 2.

The greater percentage of copper(II) ions in the zeolite can be reasonably explained as due to the presence of hydrated form of copper(II) in the zeolite. Concentrated solutions of copper(II) chloride contain $[Cu(H_2O)_4]^{++}$ ions. Although Vansant[5] reports only partial exchange of copper(II) ions in zeolites X and Y, complete exchange takes place in the case of zeolite 4A.

Acknowledgement

This work was carried out during the author's tenure as a Commonwealth Academic Staff Fellow at Imperial College, London. The author thanks Dr. L. V. C. Rees for working facilities and Dr. Arun K. Bhattacharya, F. R. I. C., F. A. I. C. for the thermal data.

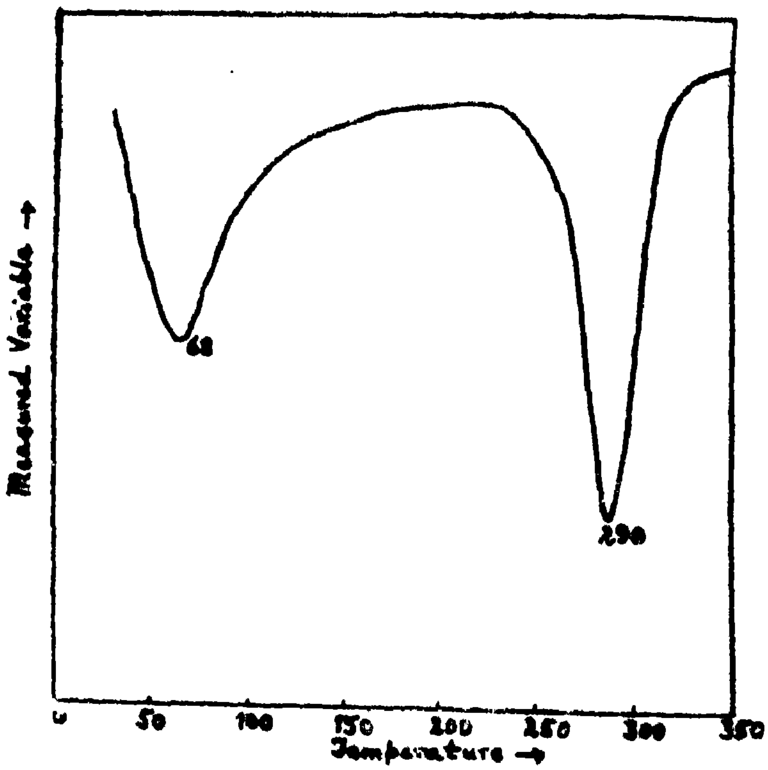


Fig. 2 : DSC of Copper zeolite

Discussion

Copper(II) zeolite displays a strong DSC endotherm at 68° and an even stronger endotherm at about 290°. Corresponding weight loss steps (15% between 0° and 290° and 14% between 290° and 650°) can be observed in the TGA curve which has an additional weight loss step around 590°. Loss of water is believed to take place atleast at the first two temperatures but decomposition, presumably of the adsorbed hydrated Cu(II), starts beyond 590°. Results of NH_4 (I)-exchange show that the zeolite is partially stable at 650°.

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Studies on molecular complexes of 8-hydroxyquinoline with potassium hexacyanoferrate(II) and potassium hexacyanoferrate(III)

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SCHILT[1] studied the 2-2'-Bipyridyl and 1, 10-Phenanthroline derivatives of potassium hexacyanoferrate(II) and potassium hexacyanoferrate(III). During the investigations on the possibility of substitution of cyano-group with 8-hydroxyquinoline in different cyanogen complexes of transitional elements, it has been observed by us that in presence of 8-hydroxyquinoline (oxine) potassium hexacyanoferrate(II) does not undergo any decomposition. When a solution of oxine in acetic acid is added to an aqueous solution of potassium hexacyanoferrate(II) and the solution slowly warmed in a waterbath, a chocolate coloured solid separates. No evolution of hydrocyanic acid takes place. This compound has been found to have the composition $K_4[Fe(CN)_6]$. 2 oxine. Identically $K_3[Fe(CN)_6]$. 2 oxine has been synthesised. These compounds are sufficiently stable towards water and acid. Oxine cannot be removed even by shaking with chloroform, alcohol and carbon tetrachloride. This is also stable at a temperature of 150° although oxine sublimes at 74°.

Experimental

All reagents used were of A. R. grade.

Analysis : The sample was fumed with a few drops of concentrated sulphuric acid and nitric acid. Then the aqueous solution of the residue was made ammoniacal when ferric hydroxide was precipitated which was filtered. Iron was estimated titrimetrically with standard potassium dichromate solution. Nitrogen was estimated by Dumas' method.

Preparation : About 2g. of potassium hexacyanoferrate(II) and potassium hexacyanoferrate(III) were separately dissolved in minimum quantity of water. The organic ligand i. e., 8-hydroxyquinoline (in the molar ratio 1 : 2) was dissolved in minimum quantity of dilute acetic acid. When these two solutions were mixed together and stirred there was immediate precipitation of chocolate brown solid for ferrate(II) and yellow solid for ferrate(III) which were filtered in sintered gooch crucible, washed with water and was finally dried to constant weight in vacuum desiccator over solid KOH. The product was obtained in about 70% yield.

Found : Fe, 8.54% ; N, 16.75%.

Calc. for $K_4[Fe(CN)_6]$, 2 oxine : Fe, 8.51% ; N, 17.02%.

Found : Fe, 9.12% ; N, 17.68%.

Calc. for $K_3[Fe(CN)_6]$, 2 oxine : Fe, 9.02% ; N, 18.3%.

Thermogravimetry :

Thermogravimetric investigations were made in T. G. Analyser of Cieco Pvt. Co. The results are plotted in fig. 1. In case of $K_4[Fe(CN)_6]$, 2 oxine

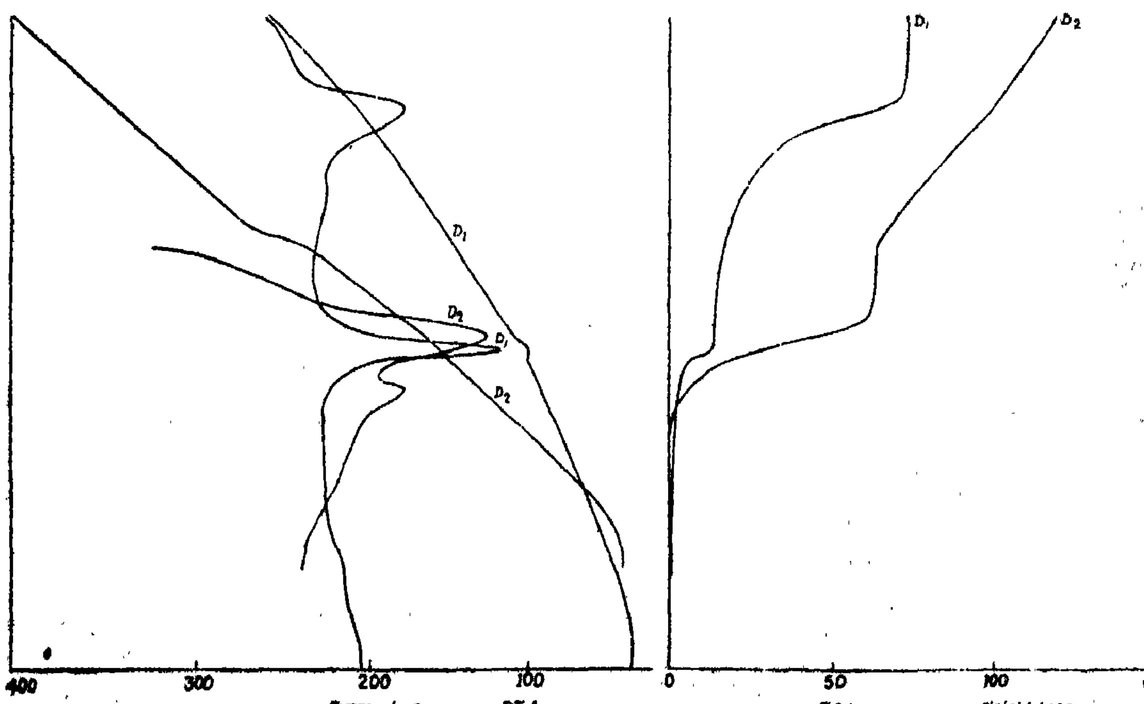


Fig. 1. Thermogravimetric analysis of $K_4Fe(CN)_6 \cdot 2oxine$ (D_1) and $K_3Fe(CN)_6 \cdot 2oxine$ (D_2)

two stable states at 160° and 185° are obtained.

	weight of the sample taken	= 140 mg.
	weight loss at 160	= 14 mg.
	weight loss at 185	= 75 mg.
Found :	weight loss at 160°	= 10%
	weight loss at 185	= 52.9%.

Net weight loss between two stable states = 42.9%.

Calculated weight loss for the final composition $K_4[Fe(CN)_6]$ = 44%.

In case of $K_3[Fe(CN)_6]$, 2 oxine only one stable state at 240 is obtained.

	weight of the sample taken	= 150 mg.
	weight loss at 240	= 64 mg.
Found :	weight loss at 240	= 42.7%.

Calculated weight loss for the final composition $K_3[Fe(CN)_6]$ = 46%

$K_4[Fe(CN)_6]$.2 oxine $\rightarrow K_4[Fe)CN)_6]$ + 2 oxine . . (1)

$K_3[Fe(CN)_6]$.2 oxine $\rightarrow K_3[Fe(CN)_6]$ + 2 oxine . . (2)

Magnetic susceptibility measurements :

Magnetic susceptibility measurements were made in Gouy balanceat 24°. The compound $K_4[Fe(CN)_6]$.2 oxine is diamagnetic (molar susceptibility λ_M (corrected) = -86.95×10^{-6}/g atom). The compound $K_3[Fe(CN)_6]$.2 oxine (with diamagnetic correction) has $\mu_{eff} = 2.839 \times (\lambda_M \times T)^{1/2} = 2.2$ B. M.

Infra-red spectra were taken in Perkin Elmer Infra-red spectrophotometer in KBr pellets. Main bands with assignments are given in Table 1.

TABLE 1

Compounds	Infra-red absorption bands (in cm^{-1})	Assignments
1. $K_4[Fe(CN)_6]$.2 oxine	570s, 700w, 750m, 820s, 1090s, 1200vw, 1300s, 1390m, 1550m, 1600s, 1680w, 2120vs, 2900-3100wb.	ν_{CN^-} 2120
2. $K_3[Fe(CN)_6]$.2 oxine	570vw, 750m, 820s, 880m, 1050w, 1090s, 1260vw, 1300s, 1390w, 1550m, 1600s, 2100s, 2900-3100wb.	ν_{CN} 2100

Reflectance spectra of compounds in solid state were taken in Hilger UVISPEK in paraffin base. Main bands with intensities are given Table 2.

TABLE 2

Compounds	ν in cm^{-1}	Intensity
1. $K_4[Fe(CN)_6]$.2 oxine	12500	w
	14700	w
	24400	m
2. $K_3[Fe(CN)_6]$.2 oxine	13700	w
	16400	m
	19200	m
	22500	sh

m = medium ; w = weak ; s = strong ; sh = shoulder , v = very ; b = broad.

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Chemical Examination of *Premna integrefolia* Linn

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PREMNA integrefolia Linn (N.O. *Verbenaceae*) is of a great value in Ayurvedic medicine. The decoction of the root is used for liver complaints, of the plant in rheumatism and neuralgia and, of leaves in cold and fever[1]. Search in literature has shown that this plant had not been examined for its crystalline principles. In the present investigation, the leaves and the stem bark have been examined.

The air dried leaves (2 Kg.) were extracted successively with *n*-hexane and ether. The hexane extract gave a dark green mass (3 gm). It did not contain any alkali solubles. So it was adsorbed over neutral alumina and eluted in succession with *n*-hexane (2 litres), and benzene (2 litres). The *n*-hexane eluate gave an yellow oil (1 gm) while the benzene eluate gave a white solid (1.5 gm), crystallizing from methanol as colourless needles [m. p. 136-138° : $(\alpha)_D^{30°}$ -36°]. The solid gave positive Libermann-Burchard test for sterols and was identified as β-sitosterol (mmp and IR). The ether extract also gave a dark green mass (1 gm) which on chromatography over alumina (eluted with benzene) gave β-sitosterol acetate (0.75 gm), crystallized from methanol as colourless needles m. p. 126-127 : $(\alpha)_D^{30°}$ -36°.

The ether extract of the stem-bark furnished only β-sitosterol while the *n*-hexane extract of the same yielded β-sitosterol and betulin. The latter crystallised from methanol in needles m. p. 248-250 (lit. 255°)[2] $(\alpha)_D$ + 19° ($CHCl_3$) ; diacetate, m. p. 210-212° ; IR : 885 and 1653 cm^{-1} (= CH_2), PMR : 5·3 τ (2H, b.S, = CH_2). In each case the identity has been established by direct comparison with the respective authentic samples.

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Existence of an Inhibitor of Iodination Reaction in Sheep Submaxillary Extract

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THE presence of iodinating enzyme(s) has been reported in some extrathyroidal tissues[1-3]. A KI-stimulated peroxidase has been partially purified from goat submaxillary gland and the preparation, although not homogeneous, exhibits both iodinase and peroxidase activities[4]. Recently, it has been shown from our laboratory that thyroxine regulates the iodinase and peroxidase activities of submaxillary gland[5]. Sheep and goat being similar species, we became interested to study the iodinating enzyme of sheep submaxillary gland. Surprisingly, it was observed that extracts of sheep submaxillary gland were unable to catalyse the formation of iodotyrosine and did not exhibit any peroxidase activity. All attempts to extract the iodinating enzyme (s) from sheep submaxillary gland including hypo- and hypertonic extraction with KCl, proteolytic digestion of crude extract, etc., failed. Thus, it was assumed that either the sheep submaxillary gland extract contains no iodinating enzyme or that an inhibitor of iodination reaction is present in it. The communication describes the presence of an inhibitor of iodination reaction in the sheep submaxillary gland.

Experimental

Fresh goat and sheep submaxillary glands were collected at the local slaughter house, cooled on ice and stored in deep-freeze. Most of the biochemicals, used in this study, were purchased from Sigma Chemical Company. The iodinating enzyme was assayed by the method of Alexander and Corcoran[6]. The reaction mixture contained, in a final volume of 3.0 ml, 200μ moles of sodium phosphate buffer of *p*H 7·0, 0·6μ mole of mono-iodotyrosine (MIT), 0.1μ mole of KI and 20 μCi of $Na^{131}I$ (carrier free), 0.5 μ mole of H_2O_2 and a suitable volume of the enzyme preparation. The reaction was started by the addition of H_2O_2 and stopped by the addition 0.2 ml of 0.01 *M* sodium thiosulphate after incubation for 20 minutes at 37°. 0.6 ml of 50% CCl_3 COOH was added and the solution kept in a boiling water bath for 3 minutes, cooled, and centrifuged at 10, 000 × g for 10 minutes. 2.0 ml aliquots of the deproteinized reaction mixture were transferred immediately to a Dowex 50 W×8 (H^+ form) column (0.8×6 cm) to determine the amount of formation of organically bound iodine as described earlier[4]. The amount of diiodotyrosine (DIT) formation was determined as described by Hati & Datta[7]. The peroxidase activity was measured according to the method of Yip[8]. Protein was estimated by the method of Lowry *et al*[9] using crystalline bovine serum albumin as standard.

All steps of enzyme preparation was carried out at 4°. A 10% homogenate of submaxillary gland was prepared with 1.16% KCl and centrifuged at 700×g in a Sorvall RC-2B refrigerated superspeed centrifuge for 15 minutes to remove cell debris and nuclei. The supernatant was used as enzyme preparation. All comparisons were made by performing parallel experiments with goat and sheep submaxillary glands under identical conditions.

Results and Discussion

The sheep submaxillary extract (SSE) showed neither iodinase nor peroxidase activity when

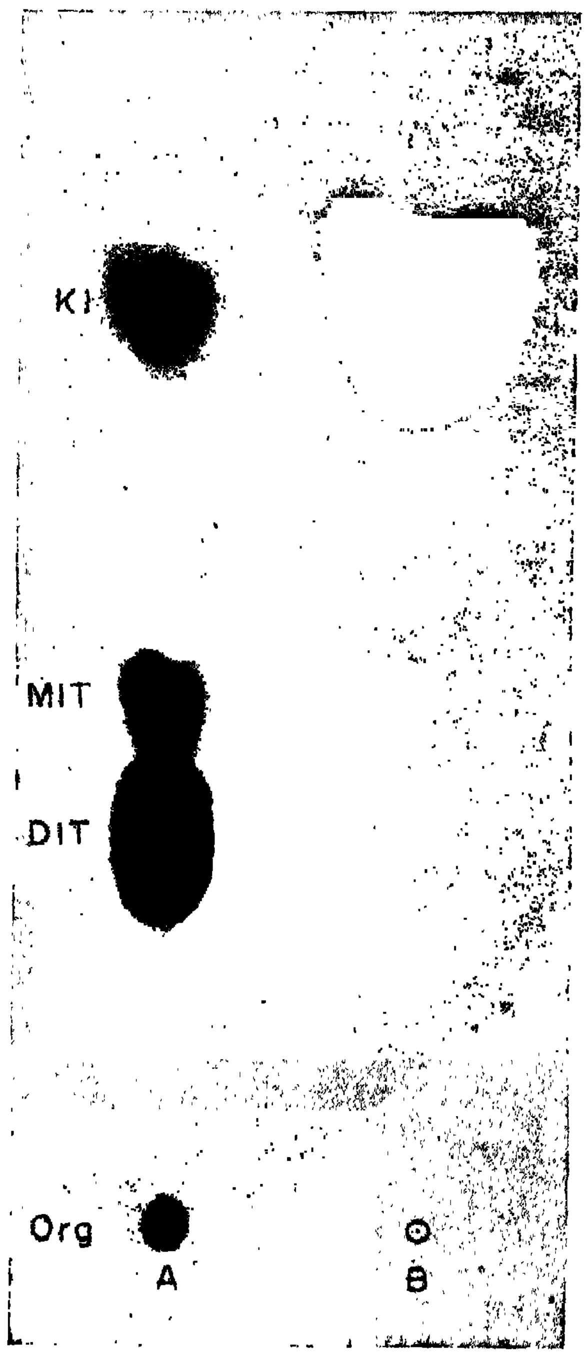


Fig. 1. Autoradiogram of the products of the reaction. A and B represent radioactive products obtained after incubation in the presence of goat and sheep submaxillary extracts respectively.

homogenized in 1.16% KCl or 0.25 *M* Sucrose or 0.05 *M* Tris-HCl buffer *p*H 7·6. On the contrary, the goat submaxillary preparation catalysed the iodination of MIT very efficiently under identical conditions (Table 1). Fig 1. describes the formation

TABLE 1—IODINATION OF MIT BY GOAT OR SHEEP SUBMAXILLARY GLAND EXTRACT

System	I^- incorporated (n moles/min/mg. protein)
Goat (0.20 mg)	21.18
Sheep (0.22 mg)	0.18
Sheep (0.44 mg)	0.22

700 × g supernatant of both goat and sheep submaxillary extracts were used in this experiment.

of DIT from MIT when the goat enzyme preparation was used. In contrast, using the sheep preparation no DIT formation could be detected. It was naturally thought that this lack of activities in SSE might be due to the absence of these enzymes or if these enzymes are present they remain in an inactive form by the presence of an inhibitor. In order to check whether our extraction procedure was efficient, the sheep submaxillary gland was extracted with various buffers of various *p*H and the extracts were treated separately with protease, trypsin, chymotrypsin, trypsin plus chymotrypsin and mild heat treatment to get the enzyme released. None of these treatments however indicated the presence of iodinase or peroxidase activities in sheep submaxillary extracts (unpublished data).

To check whether SSE contains any inhibitor of iodinase or peroxidase, iodination reaction was carried out by adding SSE to goat enzyme preparation. Table 2 shows that SSE inhibited

TABLE 2—EFFECT OF SHEEP SUBMAXILLARY EXTRACT ON THE IODINATING ACTIVITY OF GOAT SUBMAXILLARY EXTRACT

System	I^- incorporated (n moles/min/mg protein)
Goat (0.21 mg)	21.0
Goat (0.21 mg) + SSE (0.22 mg)	12 1
Goat (0.21 mg) + albumin (0.20 mg)	29 0

In this experiment 105,000 × g supernatant of both SSE and goat enzyme preparation were used as bulk of the enzyme as well as the inhibitor are present in the soluble supernatant.

the iodination of MIT catalysed by goat enzyme. The possibility that the inhibitory action of SSE might be due to a competition between iodination of MIT and the protein of SSE as protein can be iodinated. This possibility is ruled out when addition of equal amounts of albumin failed to produce any inhibition of MIT iodination (Table 2).

Addition of increasing concentrations of SSE to the goat enzyme preparation produced a progressive inhibition of MIT iodination whereas it had little effect on peroxidase activity of goat enzyme. Non-dialysability, thermolability and loss of inhibitory activity on protease treatment indicate that the inhibitor is protein in nature. None of the substrates of iodide peroxidase like MIT, KI and H_2O_2 competes with the inhibitor (Results of these experiments will be published elsewhere). However, the final proof depends on the isolation of the inhibitor in pure form. Attempts are in progress to isolate, purify and study the mode of action of this inhibitor. Although some antithyroid agents are known to inhibit the iodination reaction but no one has yet demonstrated the presence of a naturally occurring protein inhibitor which inhibits significantly the iodination reaction.

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Effect of Temperature on Non-Faradaic Electrolysis

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ONE of the authors has reported[1,2] that electrolysis of water or dilute alkali metal sulphate solution (~N/1000) at low current density (at or below 5mA/cm²) with platinum electrodes show in general three anomalies, viz.

(1) Volume deficit, (2) Ratio Anomaly, (3) Co-liberation.

These anomalies have been lately confirmed by Gosnell and Venugopalan[3] and discussed by others[3]. Such an electrolytic process has been referred to as non-Faradaic electrolysis (nFE). All previous work was done at room temperature and we have meanwhile found that temperature has a marked influence on the characteristics of nFE. Herein we present a preliminary report of the same.

Effect of Temperature

The main features of the effect of temperature on

non-Faradaic electrolysis are described below:

(1) Increase of temperature increases the extent of co-liberation i. e., the cathode gas contains a larger per cent of oxygen and the anode gas contains a larger per cent of hydrogen. In other words, there is more oxygen at the cathode and very much more hydrogen at the anode under otherwise similar conditions.

(2) But the most striking feature is the fact that co-liberation even at the anode (and the other non-Faradaic features more or less) persists up to a very high currrent density, and to some extent at a much higher concentration. For example, at room temperature the gases cease to be explosive at about 10mA/cm², whereas at 60° the gases are explosive (even) at 50mA/cm² or even higher in suitable systems. This is shown in Table 1.

idea of charged water molecules carrying the current. The observed effect of temperature naturally helps increased formation of $(H_2O)^+$ and $(H_2O)^-$ near the anode and cathode respectively. Secondly, increase of temperature increases their mobility to the corresponding opposite electrode and thus help co-liberation.

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TABLE 1

Strength	K_2SO_4 40°C i/mA	% O_2 at Cathode	% H_2 at Anode	Strength	K_2SO_4 60°C i/mA	% O_2 at Cathode	% H_2 at Anode	Strength	K_2SO_4 80°C i/mA	% O_2 at Cathode	% H_2 at Anode
0.001(N)	22	10 4**	23.3**	0.001(N)	1	31.4**	56.0**	0.001(N)	25	16.7**	29.0**
	22	13.6**	23.6**		1	32.1**	57.8**		26	17·7**	26.6**
	25	13.5**	21.6**		5	30.6**	45.9**				
	25	14 4**	22.5**		10	26.8**	38.9**				
					25	17.4**	20.5**				
0.01(N)				0.01(N)	5	33.7**	45.6**	0.01(N)			
					5	32.0**	50.2**				
	36.5	5.0*	6.1*		10	24.8**	38.5**		35	15.2**	25.0**
	36	6.0*	6.9*						39	14.8**	28.0**
	40	0.6	4.8*		40	11.4**	19.2**		40	15.6**	27.8**
	40	1.4	3.7*		45	10.4**	18.9**		41	16.0**	25.9**
					60	13.4**	22.8**		60	12.8**	23.1**
									60	12.3**	28.0**
0.1(N)	39	1.2	0.6	0.1(N)	40	1.2	1.3	0,1(N)	40	16.9**	23.7**
	39	1.0	0		41	1.1	1.3		40	16.4**	23.5**
	40	0.6	0		45	0.2	0.8		60	12.1**	15.7**
	40	0.3	0		45	0.2	0.5		60	12.9**	17.2**
									80	9.0**	6.0*
									80	9.8**	1.6

N.B.: ** means strongly explosive; * means mildly explosive; others do not explode on sparking.

Thus the limitations of low current density and low concentration which we have so far found to be essential for production of non-Faradaic features are mostly removed by an increase of temperature. Keeping concentration low (~N/1000), it is possible to increase the current density to as high as 25mA/cm² or even higher and still get explosive gases at both the electrodes or at least at the cathode. This is illustrated in Table 1. Also the concentration zone over which co-liberation takes place gets very much extended at higher temperature so much so that N/100 or even N/10 concentrations can be used to yield explosive cathode and anode gases provided the temperature iis suitably high. Thus the present work has very much extended the frontier of activity for study of non-Faradaic electrolysis.

Various theories have been suggested to explain the anomalous features of non-Faradaic electrolysis. We have critically examined all of them in a separate paper[4] and favour the one involving the

Quantitation of Copper in Some of the Copper Base Alloys by Paper Chromatographic Technique

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IN an earlier communication[1] a method of direct assessment suitable for determining uranyl ion by photodensitometer after its paper chromatographic separation was proposed. The procedure described for evaluating unknowns quantitatively from strips run simultaneously for knowns and unknowns proved better than other known methods of direct spot evaluation in paper chromatography. To apply this technique for metal ion estimations in alloys, attempts have been made in this communication to separate and estimate copper in some of the

copper base alloys. The alloys in which copper has been estimated include – silver coin (Cu, 40% ; Zn, 5% ; Ag, 50% ; Ni, 5%), monel alloy (Cu, 30·32% ; Ni, 66·9% ; Mn, 0.98% ; Fe, 1.8%), cupronickel (Cu, 68.75% ; Ni, 30.03% ; Mn, 0.86% ; rest Si, Fe, etc.), leaded brass (Cu, 59.2% ; Pb, 2.0% ; Fe, 0.045% and rest Zn), and aluminium bronze (Al, 10.8%; Mn, 0.30%; Fe, 5.58%; Cu, 83.32%, Sn and Pb, nil).

Experimental :

Preparation of alloy solutions :

A weighed quantity of the alloy (thoroughly cleaned) was taken in a small beaker (50 ml.), covered with distilled water and dissolved in nitric acid to get a clear solution by intermittent heating (if required). The excess of nitric acid was removed by careful evaporation of the solution to dryness and then the residue was extracted with distilled water. It was transferred into a 25 ml. normal flask and diluted up to the mark. Generally one gram (exactly) of the alloy was used for dissolution in 25 ml. of the solution, except in the cases of silver coin and monel alloy where the quantities taken were 1.1738 and 1.3088 gm. respectively.

Solvent System :

The solvent system used for developing and separating copper from other metal constituents of the alloys consisted of a combination of chloroform-methyl alcohol-amyl alcohol and concentrated hydrochloric acid (46 : 23 : 23 : 8 v/v). It was chosen after several preliminary studies to get spots suitable for quantitation. The Rf values of different constituent metals of the alloys investigated with this solvent system were found out experimentally as below : Cu, 0.28 ; Ni, 0.14 ; Ag, 0.0 ; Zn, 0.65 ; Pb, 0.0; Mn, 0.09 ; Al, 0.08 and Fe(III), 0.56.

Procedure : The ascending technique was used with developing chambers consisting of glass jars (height, 30 cm. ; diameter, 10 cm.) provided with well greased glass lids for making them airtight and fitted with movable glass hangers. Paper strips of Whatman No. 1 (23 × 9 cm.) were used for this work. A chromatographic technique for development of knowns and unknowns was adopted as detailed in the previous communication (loc.cit.). A time interval of ~ 2 hours was allowed for development after which the strips were taken out, dried quickly and exposed to ammonia vapours for neutralizing the acid content of the paper. These were then subjected to a spray of a 0·3% w/v solution of rubeanic acid in ethanol which formed olive green derivative with the developed spots of copper (Rf = 0.28). The colour deepened on thorough exposure of the spots to ammonia vapours. After drying, the paper strips were cut horizontally in a way suitable to get all the developed spots of the ion to be estimated. Such strips were fed to the photodensitometer (Type 201 Systronix, India) and each spot was scanned carefully and repeatedly.

The concentration of unknown (i.e., copper in the alloy sample) was estimated from calibration curves of peak heights and concentration for knowns run simultaneously with the unknown (details as per Bhatnagar et al[1]).

Using this technique quantitation of copper in the alloys listed above was carried out (see Table 1 for results).

Results and Discussion :

Though certain metal ions in alloys have been estimated by paper chromatography, yet none of these procedures is based on scanning technique as has been adopted and recommended in the present work. Thus polarography has been used to estimate cadmium in copper alloy[2] and zinc in soldering alloy[3]. Similarly colorimetry was used to estimate nickel, cobalt and copper in steel and minerals[4].

The results of the present investigations have been compared with theoretical values of copper concentrations in the alloys investigated (Table 1)

TABLE 1

Alloy	Value for Cu(II) ion in μg/drop		Error %
	Theoretical	Experimental	
Silver coin	18.75	19.50	+4.0
Cupronickel	27.50	26.00	−5.4
Monel alloy	15.10	14.50	−3.9
Leaded brass	23.70	22.50	−5.0
Aluminium bronze	33.33	32.00	−3.9

and these can be compared with any of the known instrumental methods very well. Moreover, the method adopted was quick as far as scanning or estimation step was concerned. Very small quantities (10-50 μg per drop) of the material was needed in these estimations without loss of reasonable accuracy. Thus it can be said that the suggested procedure and the chloroformic solvent used here can be adopted for routine analysis of copper in such alloys conveniently.

Acknowledgement

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Kinetics of Oxidation of Substituted Benzaldehydes by Potassium Permanganate in Acid Medium

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LITERATURE survey shows that Stewart[1] has studied the oxidation of aromatic aldehydes by $KMnO_4$ in buffer medium. It was also observed[2] that oxidation of substituted benzaldehydes by permanganate undergoes general acid catalysis. The observed results showed that the general acid catalysis was of the order pyrophosphate>dihydrogen phosphate>acetate. As an extension of the work, the oxidation of substituted benzaldehydes by $KMnO_4$ in H_2SO_4 medium, was made in order to study the various factors that affect the rate of reaction and also to propose a suitable mechanism.

Experimental

All the chemicals used were BDH (AnalaR) grade. Acetic acid was once refluxed over Chromium trioxide and twice distilled over $KMnO_4$. The middle fraction boiling at 117°-118° (literature value 118·5°) was used. An Elico *p*H meter Model LI-10 and Spekol colorimeter were used for determining *p*H and optical density respectively. The reaction was followed iodometrically as well as by colorimetric method due to disappearance of MnO_4^- at 527 nm.

Results and Discussion

The stiochiometry of the reaction was found to be 2 moles of MnO_4^- to 5 moles of X-C_6H_4 CHO and the product was identified as X-C_6H_4-COOH. This can be explained by the following stiochiometric equation

$$5\ RCHO + 2MnO_4^- + 6H^+ \rightarrow 5\ RCOOH + 2Mn^{++} + 3H_2O$$

The reaction was found to be first order in aldehyde and in permanganate respectively. The overall second order rate constant k_2 was calculated using the equation[3]. The rate constants were determined in 1*M* H_2SO_4 in the temperature range between 15° to 30° and thermodynamic parameters are given in Table 1.

In aqueous acetic acid medium, rates were studied at different percentages of acid. The rate increased with decreasing dielectric constant suggesting that the reaction is of ion-dipole type. The rate constants for substituted benzaldehydes in acetic acid are given in Table 2.

TABLE 1

RATE CONSTANTS AT DIFFERENT TEMPERATURES AND THERMODYNAMIC PARAMETERS

$[RCHO]_0 = 8.0 \times 10^{-4} M$; $[KMnO_4]_0 = 4.0 \times 10^{-4} M$: Temperature = 25°C
$H_2SO_4 = 1M$

Substituent	(Kl.m.$^{-1}$ sec^{-1}) 15°	20°	25°	30°	35°	$\Delta E^{\neq}$ (K.cals/mole)	$\Delta H^{\neq}$ (K.cals/mole)	$-\Delta S_{\neq}$ (e.u)
o-NO_2	0.54	8.77	1.06	1.44	1.93	11.4	10.8	22.2
p-OH_3	0.40	0.56	0.77	1.25	1.86	12.88	11.7	19.8
–H	0.85	0.50	0.70	0.86	1.12	11.4	10.8	23.0
2, 6-Cl_2	0.88	0.47	0.64	0.84	1.10	9.9	9.3	28.9
o-Cl	0.82	0.46	0.58	0.81	1.02	10.1	9.5	27.8
p-Cl	0.30	0.40	0.53	0.76	0.98	10.9	10·3	25.2
p-NO_2	0.25	0.34	0.48	0.60	0.82	10.5	9.9	26.8
m-Cl	0.20	0.25	0.34	0.40	0.53	9.1	8.5	32.2
m-NO_2	0.16	0.19	0.24	0.27	0.34	6.8	6.2	40.9

TABLE 2

SOLVENT EFFECT

$[RCHO]_0 = 8.0 \times 10^{-4} M$; $[MnO_4^-]_0 = 2.0 \times 10^{-4} M$
K(l.m.$^{-1}$ sec^{-1})

Substituent	Temperature (°C)	Percentage of acetic acid V/V 10	20	30	40	50
o-NO_2	32	0.48	0.47	0.60	1.28	2.50
p-CH_3	32	0.25	0.42	0.50	0.93	1.40
-H	29	0.11	0.14	0.17	0.46	1.30
2, 6-Cl_2	28	0.82	0.40	0.77	1.88	3.66
o-Cl	32	0.37	0.46	0.59	1.07	1.72
p-Cl	27	0.16	0.22	0.37	0.80	1.85
p-NO_2	32	0.32	0.48	0.52	0.96	2.30
m-Cl	27	0.62	0.70	0.92	1.00	3.40
m-NO_2	32	0.40	0.45	0.58	1.12	2.34

The Hammett's plot for the oxidation of substituted benzaldehydes by $KMnO_4$ in 1*M* H_2SO_4 at 25° gives a straight line with a slope $\rho = -0{\cdot}70$. This shows that electron releasing substituents in the benzene ring accelerate the rate of reaction while electron withdrawing substituents retard the rate. This also indicates an electron deficient transition state. Since both meta and para substituents fit into the above plot, the resonance effect of the para substituent is probably small. However *p*-NO_2 compound deviates appreciably indicating a strong resonance interaction. It is also of interest

to discuss the effect of ortho-substituents on the reaction mechanism. Although the polar effects of ortho-substituents are generally recognised to be equal to those of para-substituents, the ortho-substituents in some case produce a large rate-enhancement as was observed by Vankatasubramanian[4]. Jayaraman[5] while investigating the proximity and cumulative effect in the chromic acid oxidation of substituted benzaldehydes has observed the rate retardation with *ortho-substituents* because of steric hindrance. *But* our results using $KMnO_4$ as an oxidant indicates a reverse trend viz. *o*-NO_2>*p*-NO_2>*m*-NO_2 in nitro series and 2,6-Cl_2>*o*-Cl>*p*-Cl>*m*-Cl in chloro series. This shows that steric hindrance is not of much importance. The plot of ΔH^* versus ΔS^* was linear with a slope equal to $\beta = 2401$ K. This linear relationship indicates that all the substituted compounds studied follow the same type of mechanism. In order to find whether specific acid catalysis occurs, the experiments were conducted in concentrated H_2SO_4 and $HClO_4$ acid medium at different concentrations viz. 0·5 to 3.0*M*. The rate increases with increasing acid concentration and order with respect to H^+ is one upto 2.0 *M*. Bunnett's[6] plot of $(\log k + H_0)$ versus $\log {}^aH_2O$ gave a straight line with slope 'w' equal to 6.5. Bunnett formulated that the 'w' values lying between 3.1 to 6.8. suggest a mechanism involving water molecule acting as a proton transfer agent. This can be explained by the following mechanism.

$$RCHO + MnO_4^- + H^+ \rightleftharpoons R-\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}-O-MnO_3$$

$$R-\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}-O-MnO_3 + H_2O \xrightarrow{\text{Slow}} RCOOH + H_3O^+ + MNO_3^-$$

$$5MnO_3^- + 6H^+ \xrightarrow{\text{Fast}} 3MnO_4^- + 2Mn^{+2} + 3H_2O$$

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New Mannich Bases from 5-(Methyl phenoxymethyl)-1, 3, 4-oxadiazol 2-thione derivatives and their Bactericidal Properties

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THE herbicidal[1], bactericidal[2-4] and insecticidal[5,6] properties exhibited by oxadiazole compounds have made them of considerable interest specially in the field of pesticide chemistry. An effective insecticide based on oxadiazole moiety, against houseflies and cockroaches was patented[7]. Many Mannich bases have been reported to possess antibacterial[8], fungicidal[9] and anticonvulsant[10] properties. In view of these observations a series of 3-arylaminomethyl-5-(methylphenoxymethyl)-1, 3, 4-oxadiazol 2-thione derivatives have been synthesised to study their bactericidal properties.

The key intermediates 5-methylphenoxymethyl 1, 3, 4-oxadiazol-2-thiones prepared by the method of Young and Wood[11] were subjected to Mannich reaction according to procedure earlier reported in the literature[12,13].

The desired Mannich bases were isolated by two methods as described in the experimental.

The IR spectra of the Mannich bases showed the presence of C=S bands as sharp and strong peaks in the region of 1050-1090 cm^{-1}.

Experimental

Melting points were taken in open capillary tubes and are uncorrected. Infra-red spectra were taken in a Perkin-Elmer spectrophotometer in KBr pellets.

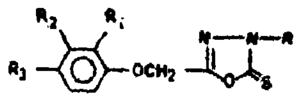
5-(4-methylphenoxymethyl)-1, 3, 4-oxadiazol-2-thione (Ie)

A suspension of 0.1 mole of 4-methylphenoxy acetyl hydrazide, 0.1 mole of potassium hydroxide and 0.11 mole of carbon disulfide was refluxed on steam bath for 12 hours. The reaction mixture was cooled, solvent distilled off and residue dissolved in water and filtered. The clear filtrate was acidified with dilute hydrochloric acid and the separated solid was crystallised from ethanol to afford the compound (Ie). The other two compounds (Ia, Ic) were similarly prepared (analytical data vide Table 1).

3-Hydroxymethyl-5(4-methyl phenoxymethyl)-1, 3, 4-oxadiazol-2-thione (If)

To a suspension of compound (Ie ; 0.1 mole) in 100 ml ethanol was added formaldehyde (40% ; 1.0 g). The reaction mixture was left overnight at room temperature, the separated solid was filtered and crystallised from ethanol to furnish compound (If). Two other compounds (Ib, Id) were prepared according to the same procedure (analytical data vide Table 1).

TABLE—1



I

S.N.	Structure I R	R_1	R_2	R_3	M.P. °C	Molecular formula*	Yield %
a.	H	CH_3	H	H	121	$C_{10}H_{10}N_2O_2S$	54
b.	CH_2OH	CH_3	H	H	100-1	$C_{11}H_{12}N_2O_3S$	90
c.	H	H	CH_3	H	96-7	$C_{10}H_{10}N_2O_2S$	50
d.	CH_2OH	H	CH_3	H	79	$C_{11}H_{12}N_2O_3S$	87
e.	H	H	H	CH_3	149	$C_{10}H_{10}N_2O_2S$	60
f.	CH_2OH	H	H	CH_3	124	$C_{11}H_{12}N_2O_3S$	90

" Elemental analyses (N) were within ±0.4% of the theoretical value.

3-Substituted aminomethyl-5-(methyl phenoxymethyl)-1, 3, 4-oxadiazol-2-thiones (II)

Method A : A solution of 3-hydroxymethyl-5-methylphenoxymethyl-1, 3, 4-oxadiazol-2-thione (0.01 mole) and aromatic amine (0.01 mole) in 25 ml of ethanol was kept overnight in a refrigerator. The separated solid was filtered and crystallised from ethanol-acetone mixture.

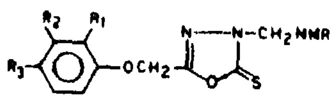
Method B : To ethanolic solution of 5-methylphenoxymethyl-1, 3, 4-oxadiazol-2-thione (0.01 mole) and formaldehyde (40% ; 1 g), an ethanolic solution of aromatic amine (0.01 mole) was added slowly with stirring. The reaction mixture was left at room temperature for 12 hours, when a colourless solid was obtained which was filtered and crystallised from excess ethanol.

Compounds(II) prepared according to these two methods are presented along with relevant data in Table 2.

Biological data

The compounds(II) as recorded in table 2 were

TABLE—2



II

S. No.	R	R_1	R_2	R_3	Method	M.P. °C	Molecular formula[f]	Yield %	Antibacterial activity against* *E. coli*	*B. magaterium*	*S. typhi*	*S. aureus*
1.	Phenyl	CH_3	H	H	B	141	$C_{17}H_{17}N_3O_2S$	65	−	+	++	+
2.	4-Chlorophenyl	CH_3	H	H	A	152	$C_{17}H_{16}ClN_3O_2S$	65	+	+	++	++
3.	3-Chlorophenyl	CH_3	H	H	A	105	$C_{17}H_{16}ClN_3O_2S$	56	+	+	++	++
4.	2-Chlorophenyl	CH_3	H	H	B	110	$C_{17}H_{16}ClN_3O_2S$	58	+	+	+	+
5.	4-Bromophenyl	CH_3	H	H	A	159-60	$C_{17}H_{16}BrN_3O_2S$	64	++	+	+	+
6.	4-Tolyl	CH_3	H	H	A	148-49	$C_{18}H_{19}N_3O_2S$	60	+	++	+++	+
7.	2-Naphthyl	CH_3	H	H	A	150	$C_{21}H_{19}N_3O_2S$	50	−	+	−	−
8.	4-Anisyl	CH_3	H	H	B	127	$C_{18}H_{19}N_3O_3S$	58	+	+	++	+
9.	4-Nitrophenyl	CH_3	H	H	A	140-1	$C_{17}H_{16}N_4O_4S$	56	−	−	+	+
10.	Phenyl	H	CH_3	H	B	98	$C_{17}H_{17}N_3O_2S$	56	+	+	+	+
11.	4-Chlorophenyl	H	CH_3	H	A	131	$C_{17}H_{16}ClN_3O_2S$	60	++	+	+	++
12.	4-Bromophenyl	H	CH_3	H	B	129-30	$C_{17}H_{16}BrN_3O_2S$	62	+	+	++	+++
13.	4-Tolyl	H	CH_3	H	A	132	$C_{18}H_{19}N_3O_2S$	61	++	+	+	++
14.	4-Anisyl	H	CH_3	H	A	137	$C_{18}H_{19}N_3O_3S$	58	+	++	+	+
15.	4-Nitrophenyl	H	CH_3	H	A	146	$C_{17}H_{16}N_4O_4S$	58	+	+	+	+++
16.	3-Nitrophenyl	H	CH_3	H	B	148-49	$C_{17}H_{16}N_4O_4S$	54	+	−	+	++
17.	2-Naphthyl	H	CH_3	H	A	144	$C_{21}H_{19}N_3O_2S$	50	−	−	−	+
18.	Phenyl	H	H	CH_3	B	106-7	$C_{17}H_{17}N_3O_2S$	70	++	+	+++	+++
19.	4-Chlorophenyl	H	H	CH_3	B	130-1	$C_{17}H_{16}ClN_3O_2S$	70	++	+	+++	+++
20.	3-Chlorophenyl	H	H	CH_3	A	113-14	$C_{17}H_{16}ClN_3O_2S$	62	++	++	+	+++
21.	2-Chlorophenyl	H	H	CH_3	A	115	$C_{17}H_{16}ClN_3O_2S$	60	+	+	+	++
22.	4-Bromophenyl	H	H	CH_3	B	128	$C_{17}H_{16}BrN_3O_2S$	68	+	−	++	++
23.	4-Tolyl	H	H	CH_3	B	85	$C_{18}H_{19}N_3O_2S$	68	+	++	++	+++
24.	2-Tolyl	H	H	CH_3	A	151	$C_{18}H_{19}N_3O_2S$	60	++	−	++	++
25.	4-Anisyl	H	H	CH_3	B	134	$C_{18}H_{19}N_3O_3S$	62	+	+	+	++
26.	4-Nitrophenyl	H	H	CH_3	B	163	$C_{17}H_{16}N_4O_4S$	62	+	+	+	−
27.	3-Nitrophenyl	H	H	CH_3	A	131-32	$C_{17}H_{16}N_4O_4S$	58	+	−	−	−
28.	2-Naphthyl	H	H	CH_3	A	110	$C_{21}H_{19}N_3O_2S$	55	−	−	−	−

f = Elemental analyses (N) were within ±0.4% of the theoretical value.

* − = No inhibition ; + = Zone size 6-8 mm ; ++ = Zone size 8-10 mm ; +++ = Zone size greater than 10 mm.

screened for their inhibitory effects against four organisms viz., *Escherichia coli*, *Salmonella typhosa*. *Staphylococcus aureus* and *Bacillus magaterium* by agar diffusion techniques[14].

The agar medium was inoculated with a 24 hour old culture of the test organism. Filter paper discs (5 mm diameter) saturated with the test compounds (10 mg/ml in acetone) were placed on the agar plate after drying up the solvent. After an incubation period of 24 hours the zones of inhibition around the discs were measured (Table 2.)

Most of the compounds were found to exhibit activity. Significant activity against *S. aureus* was shown only by compound No. 12, 15, 18, 19, 20 and 23. Only three compounds (6, 18 and 19) showed marked inhibition against *Salmonella typhosa*. Bacterial cultures maintained at C.D.R.I., Lucknow were used.

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Thermal Stability of Gd_2CuO_4

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The thermal stability of Gd_2CuO_4 as a function of oxygen potential in the gas phase has been studied by thermogravimetry. It is observed that Gd_2CuO_4 decomposes first to an intermediate phase Gd_2CuO_{4-x} and finally to Gd_2O_3 and Cu_2O.

The standard free energy change, $\Delta G^{o}_{O_2}$ data was derived only from the decomposition steps during heating the mechanism of decomposition and reformation is verified by X-ray diffraction analysis of the products at various stages.

RARE earth copper oxides of the general formula Ln_2CuO_4 were shown to exhibit very interesting electrical properties[1], besides their remarkable catalytic and magnetic behaviour[2]. Rare earth oxides and copper oxides were shown to form compounds of the type Ln_2CuO_4[1] (Ln = La, Nd, Sm, Eu, Gd), $Ln_2'Cu_2O_5$[3] (Ln' = Tb, Dy, Er, Yb, Y) and Ln″. CuO_2(Ln″ = La, Pr, Nd, Sm, Eu). The standard Gibbs' free energies of formation of the Ln_2CuO_4 and $Ln_2'Cu_2O_5$ were determined by Tretyakov et al[3] by oxide electrolyte cell method. These authors[3] agreed that Ln″CuO_2 compounds were unstable above 1273 K and therefore assumed the phase Cu_2O to be coexisting with Ln_2O_3, Ln_2CuO_4 or $Ln_2'O_3$, $Ln_2'Cu_2O_5$ in order to fix the oxygen potential in the range 1200-1350 K. However, independent investigations carried out earlier in this laboratory[4,5] on La_2CuO_4 using similar galvanic cell method over an extensive temperature range (970-1370 K) clearly established the fact that it is $LaCuO_2$ and not Cu_2O that should coexist with La_2O_3 and La_2CuO_4. Lehuede[6] et al showed that when La_2CuO_4 is heated under vacuum at 1023 K, a non-stoichiometric phase, La_2CuO_{4-x}, is obtained. Haas and Kordes[7] reported that Gd_2O_3 did not form $GdCuO_2$ and probably the thermal stability of $LaCuO_2$ decreased from La to Eu such that $GdCuO_2$ could not be formed. Hence a thermogravimetric study of Gd_2CuO_4 in controlled atmosphere was undertaken.

Experimental

Materials: Reagent grade Gd_2O_3 (from Indian Rare Earths) and copper acetate (E. Merck, A.R. grade) were used as starting materials. A coprecipitation followed by solid state reaction method[1] was adopted for the preparatin and Gd_2CuO_4 obtained was characterized by X-ray diffraction technique.

Thermogravimetric analysis was carried out on Stanton thermobalance (Model HT). Four different oxygen partial pressures in the range 0.0213 to 0.0022 MPa were obtained by appropriate mixing of compressed air and nitrogen through Fisher mixing flowmeters. Flow rates were in the range 2-12 $cm^3 sec^{-1}$. Temperature calibration was carried out by comparison of the CuO decomposition temperatures at different P_{O_2}. Philips X-ray unit, PW 1010 alongwith Diffractometer PW 1051 was used for X-ray diffraction analysis of different products.

Results and Discussion

According to Tretyakov[3] Gd_2CuO_4 (or any Ln_2CuO_4) should decompose in air according to the equation (1) :

$$Gd_2CuO_4 \rightleftharpoons Gd_2O_3 + \tfrac{1}{2}Cu_2O + \tfrac{1}{4}O_2 \quad \dots (1)$$

In the case of La_2CuO_4 it was established that the decomposition proceeds[4,5] according to (2) and (3) :

$$La_2CuO_4 \rightleftharpoons LaCuO_2 + \tfrac{1}{2}La_2O_3 + \tfrac{1}{4}O_2 \dots (2) \quad (970\text{-}1370\ K)$$

$$LaCuO_2 \rightleftharpoons \tfrac{1}{2}La_2O_3 + \tfrac{1}{2}Cu_2O \quad \dots (3) \quad (1370 < T \leqslant 1473\ K)$$

If Gd_2CuO_4 should completely decompose into Gd_2O_3 and Cu_2O, even then percentage weight loss should be less than 2% ; this would necessitate taking large amounts (~500 mg) of the sample. However, very large amounts of the sample (2-3 g) though yielded a better measurement of weight loss could introduce serious ambiguities in initiation temperature for the reasons discussed[8] elsewhere. Normally 500-700 mg sample was used for each run except those intended exclusively for determination of compositions. Gd_2CuO_4 underwent decomposition in two steps (4) and (5) :

$$Gd_2CuO_4 \rightleftharpoons Gd_2CuO_{4-x} + \tfrac{x}{2}O_2 \quad \dots (4)$$

$$Gd_2CuO_{4-x} \rightleftharpoons Gd_2O_3 + \tfrac{1}{2}Cu_2O + \frac{0.5-x}{2}O_2 \dots (5)$$

By taking large amount of sample x was estimated to be 0.30-0.40. Absolute value of the oxygen/metal ratio of the quenched sample of

Gd_2CuO_{4-x} was established by H_2-reduction into Gd_2O_3 and Cu metal using a precise microthermo-balance[4]. The composition was found to be $Gd_2CuO_{3.65}$.

When the second stage of decomposition is complete, the products were cooled in flowing N_2 (oxygen content 3000 ppm) and characterised by X-ray powder patterns. The products were mainly Cu_2O and Gd_2O_3 with traces of Gd_2CuO_4 (due to reoxidation by oxygen impurity in N_2). The intermediate Gd_2CuO_{4-x} was found to be an entirely new phase hitherto unreported.

The TG runs were taken in both static and flowing air (flowrate 12 cm^3sec^{-1}) environment. Understandably flowing air registered 10-15° lower temperatures than static air. Several thermal cycles were conducted on the same sample. The most remarkable feature of this investigation was the high degree of reversibility of the reactions (4) and (5) in oxygen rich environments (at heating or cooling rates of 4-6° min^{-1}). Since cooling curves gave rise to much larger uncertainties in temperature (±20°) compared to heating curves (±10°) only the latter were considered for further evaluation. Table 1 represents the summary of data from those runs which did not show kinetic limitations. It is seen that at the four oxygen partial pressures employed (0.0218, 0.049, 0.0914 and 0.21 in units of 0.101 MPa), the calculated RT ln P_{O_2} showed a fairly linear dependance with temperature (Table 2 and Fig. 1)

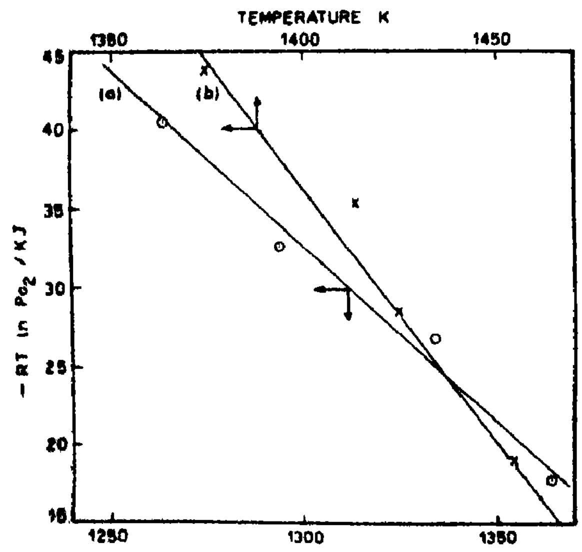


Fig. 1 RTln P_{O_2} vs T Plot for the System
(a) $Gd_2CuO_4 \rightarrow Gd_2CuO_{4-x}$ (⊙)
and (b) $Gd_2CuO_{4-x} \rightarrow Gd_2O_3Cu_2O$ (X)

for both the reactions (4) and (5). Lower oxygen partial pressures (e. g., N_2 with 3000 ppm oxygen) did not yield any useful data owing to kinetic limitations.

The standard Gibb's free energy change for reactions (4) and (5) could be represented by the linear equations (6) and (7) :

TABLE 1

VARIATION OF DISSOCIATION TEMPERATURES WITH LN P_{O_2}

Volume flow rate $dm^3\ hour^{-1}$ Air	N_2	P_{O_2}(a)	ln P_{O_2}	T_1/K	T_2/K
4.62	40.0	0.0218	−3.88	1268	1378
4.62	15.4	0.049	−3.02	1298	1418
4.62	6.0	0.0914	−2.39	1338	1428
9.0	0.0	0.21	−1.56	1363	1453(b)

TABLE 2

FREE ENERGY DATA FOR Gd_2CuO_4

T_1/K	$\Delta G°$/KJ(c)	T_2/K	$\Delta G°$/KJ(c)
1268	40.2	1378	43.7
1293	32.5	1418	35.5
1338	26.5	1428	28.3
1363	17.7	1453	18.8

(a) With reference to pure oxygen at a pressure of 0.1013 MPa.

(b) In static air, the decomposition temperatures are higher for obvious reasons.

(c) For the reaction producing 1 mole of oxygen.

(d) T_1 and T_2 represent the temperatures of the two decomposition steps.

$$\Delta G^\circ_{O_2} \pm 5/KJ = -323 + 0.225\ T\ (1263\text{-}1363\ K) \quad ...(6)$$

$$\Delta G^\circ_{O_2} \pm 5/KJ = -476 + 0.314\ T\ (1373\text{-}1453\ K) \quad ...(7)$$

Owing to very limited temperature range equations (6) and (7) represented free energy data strictly over the temperature range of experiment ; these should not be extrapolated to identify the intercept and slope as enthalpy and entropy changes[5] respectively especially so for a dynamic technique. However, it is interesting to compare with the only equilibrium measurement available on this system by Tretyakov et al[8]. They measured the emf of the cell

$$Pt,\ Gd_2CuO_4,\ Gd_2O_3,\ Cu_2O/ZrO_2(Y_2O_3)/O_2(air)Pt \quad ...(8)$$

over 1220-1360 K which could be represented by the least square equation (9)

$$E \pm 1/mV = 607.3 - 0.418\ T \quad ...(9)$$

The temperature at which the dissociation pressure of "Gd_2CuO_4" equals P_{O_2} of air, emf of the above cell should be zero. Therefore equation (9) to zero, temperature of dissociation works out to be 1453 K. This extrapolated value (1453 K) is identical with our value (Table 2) for the second reaction (i. e., Gd_2CuO_{4-x} to Gd_2O_3 and Cu_2O). This agreement is of course fortuitous as could be seen by calculation of temperature at which P_{O_2} of the ternary electrode in cell (8) equals 0.0022 MPa

(the lowest P_{O_2} of the present TG study, Table 1); it is 1300 K in contradiction with observed values of 1263 and 1363 K quoted in Table 1 for the reactions (4) and (5) respectively. Since equation (9) by Tretykov et al[3] corresponded to reaction (1) by virtue of their choice of solid phase to fix the P_{O_2}, it [equation (9)] should be an average situation of the equilibria (4) and (5).

To conclude, this investigation clearly established that Gd_2CuO_4 decomposes into Gd_2O_3 and Cu_2O through a new intermediate phase Gd_2CuO_{4-x} which was isolated and characterized using dynamic TG method, the thermodynamic dependence of ambient P_{O_2} (in the range 0.0213 to 0.0022 MPa) on initiation temperature of reactions (4) and (5) could be determined. This compound proves to be one of the rare example of the reversible solid solid reaction.

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The Thermal Decomposition of Oxyhyponitrites of Barium and Potassium

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Barium and potassium oxyhyponitrites are found to behave exactly alike and like the sodium salt : nitrogen(I) oxide is the main gaseous product in all the three cases. No nitric oxide is produced except if the nitrite produced decomposes. Nitrate is formed though no nitric oxide is present in the products.

THE preparation and decomposition of oxyhyponitrites of sodium, calcium, barium, strontium, and lead is very sparsely reported[1,2]. The sodium salt is stated to decompose as $2Na_2N_2O_3 \rightarrow Na_2N_2O_2 + 2NaNO_2^2(1)$ followed by $3Na_2N_2O_3 \rightarrow 2Na_2O + 2NaNO_2 + 2N_2^1$ (2) and all the rest as $M_2N_2O_3 \rightarrow M_2O + 2NO^1$(3). The sodium salt reported by Oza[3] and by Oza and Dipali[4] decomposed as $2Na_2N_2O_3 \rightarrow 2NaNO_2 + Na_2O + N_2O$(4).

The theory of decomposition or hyponitrites[3], of oxynitrogen salts[4] and mode of linkage of oxygen in these oxy-salts[5] need studies on these salts. Quantitative similarity in the behaviour of sodium hyponitrite and oxyhyponitrite is reported in Oza and Dipali[4]. It now emerges that the oxy-salts of sodium, potassium and barium behave identically and *not* differently as reported earlier.[1]

Experimental

Technique of work was the same[4]. Heating was done ultimately till cessation of gas evolution to ensure decomposition of all hyponitrite and oxyhyponitrite. Barium and potassium salts were prepared by double decomposition using the sodium salt ; both were monohydrates.[1] Found : K, 45.95 ; N (Dumas) 16.28 ; Ba, 59.29 ; N, 12.10%. $K_2N_2O_3$, H_2O requires K, 45.35;N,16.30; $BaN_2O_3H_2O$ requires Ba, 59.31 ; N, 12.12%. Nitrogen(I)oxide was first absorbed out in cold alcohol satd. with nitric oxide and residual gas tested for presence of nitrogen(II)oxide with satd. $FeSO_4$soln. K_2O was removed from the solid residue by shaking repeatedly with alcohol and the material left dissolved in water. The residue of barium salt was dissolved in water ; the addition of $AgNO_3$ aq. to this indicated presence of traces of hyponitrite. Oxide was titrated with succinic acid, nitrite with permanganate and total nitrate as in ref. 7. The traces of hyponitrite present were removed prior to estimation by boiling[9] since nitrites are stable in such solutions[8].

Results and Discussion

The table shows results obtained when weighed amounts were decomposed in vacuo at temperatures stated. The gas stated under (*b*) was obtained at the higher temperature until gas evolution ceased. Results 1-10 for barium salt and 11-23 for potassium salt, being similar, are reviewed collectively. Except at 550° no nitrogen(II)oxide is present : the presence of oxygen confirms this (Exp. 23). Note that oxygen is evolved first and nitric oxide next. Nitrogen(I)oxide is the major gas while oxide and nitrite major solid products. When abruplty decomposed, production of nitrogen and nitrate increases. The amounts of nitrite and oxide produced do not bear relation to the amount of oxy-salt decomposed (Exps. 1-4) but the ratios (*a*) oxide formed to oxy-salt decomposed, (*b*) nitrite formed to oxy-salt decomposed are approximately constant.

Evidently nitrogen(II)oxide is not a product : so eq.(1) is dismissed.[1] Oxygen is evolved first and nitrogen(II)oxide next : intermediate peroxide formation is favoured[3]. The formation of nitrogen(I)oxide and nitrite – major products – is also readily explained on intermediate production of metal peroxide. Thus—

$$M_2N_2O_3 \rightarrow M_2O_2 + N_2O \quad \ldots \text{ I}$$

$$M_2N_2O_3 + M_2O_2 \rightarrow 2MNO_2 + M_2O_2 \quad \ldots \text{ II}$$

Oxygen is formed from M_2O_2(I) while NO from MNO_2(II), the latter only when temperature is suitably high.

The disproportionation reaction of Angeli[8], occurring side by side with decomposition, explains the production of nitrogen.

$$2M_2N_2O_3 \rightarrow M_2N_2O_2 + 2MNO_2 \quad \ldots \text{ III}$$

$$M_2N_2O_2 \rightarrow M_2O_2 + N_2 \quad \ldots \text{ IV}^3$$

Metal peroxide formed in(IV) exercises cheque on

TABLE—THE THERMAL DECOMPOSITION OF BARIUM OXYHYPONITRITE AND POTASSIUM OXYHYPONITRITE

Exp. No.	Mass (mg)	Time (mt)	Temp. °C	Lot No.	Gas(ml) Total	NO	N_2O	O_2	N_2	NO_2/N_2O_3	Solid residue(mg.) Oxide	Nitrite	Nitrate	Ratios BaO/BaN_2O_3	$Ba(NO_2)_2$/BaN_2O_3
1	25.00	—	255		1.2	nil	0.65 (53.8)	nil	0.55	nil	6.1	13.8	2.00	0.27	0.60
2	50.60	—	,,		2.9	,,	2.0 (70.0)	,,	0.90	,,	12.8	27.5	3.0	0.28	0.00
3	75.00	—	,,	a	1.8	,,	1.4 (77.7)	0.1	0.30	,,					
			350	b	2.4	,,	1.6 (66.6)	0.15	0.65	,,	20.3	38.5	5.6	0.30	0.56
4	150.00	—	255-350		7.9	,,	4.2 (54.0)	0.1	3.6	,,	40.5	65.4	20.00	0.29	0.47
5	250.00	—	255	a	2.7	,,	2.00 (66.0)	nil	0.7	,,					
			255	a	2.2	,,	1.4 (63.6)	,,	0.8						
			255	a	4.1	,,	1.8 (44.0)	,,	2.3						
			255	a	3 6	,,	1.5 (41.2)	,,	2.1						
			350	b	0.2	,,	0.08	,,	0.12		66.2	111.8	39.00	0.29	0.48
6	300.00	—	255	a	4.2	,,	3.2 (76.2)	0.15	0.85	,,					
			255	a	1.8	,,	1.2 (66.7)	nil	0.6						
			255	a	0.9	,,	0.55 (61.1)	,,	0.35						
			255	a	5.8	,,	3.0 (51.7)	trace	2.8						
			350	b	2.2	,,	0.6 (21.0)	0.1	1.5						
7	100.00	15	255	a	1.6	,,	0.9 (56.2)	nil	0.7	,,					
			350	b	3.6	,,	2.8 (77.7)	trace	0.8						
8	100.00	30	255	a	2.6	,,	2.1 (50.0)	nil	0.5	nil					
			350	b	2.7	,,	2.0 (74.0)	0.2	0.5	,,					
9	100.00	45	255	a	4.4	,,	3.0 (69.0)	nil	1.4	,,					
			350	b	0.8	,,	0.55 (69.0)	,,	0.25	,,					
10	100.00	60	255	a	3.1	,,	2.1 (71.0)	0.15	0.85	,,					
			255	a	2.3	,,	1.5 (65.2)	0.2	0.60	,,					
			350	b	0.65	,,	0.4 (61.6)	trace	0.20	,,					
	$K_2N_2O_3, H_2O$:														
11	100.00	15	260	a	2.1	nil	1.1 (52.4)	nil	1.0	nil					
			400	b	3.0	,,	2.4 (80.0)	,,	0.6	,,	28.7	49.5	1.32	0.32	0.5
12	100.00	30	260	a	2.7	,,	1.45 (53.7)	,,	1.25	,,					
			400	b	2.7	,,	2.05 (83.3)	,,	0.65	,,	28.9	50.1	1.34	0.32	0.56
13	100.00	45	260	a	3.6	,,	2.25 (62.5)	,,	1.35	,,					
			400	b	1.8	,,	1.15 (63.9)	,,	0.65	,,	28.6	50.5	1.29	0.32	0.56
14	100.00	60	260	a	3.8	,,	2.5 (67.6)	,,	1.3	,,					
			400	b	1.15	,,	0.75 (65.2)	,,	0.4	,,	28.5	50.5	1.34	0.32	0.56
15	51.00	—	250	—	2.9	,,	1.8 (62.1)	,,	1.1	,,					
16	76.20	—	240	—	4.45	,,	3.2 (71.0)	,,	1.25	,,					

(Contd. Table)

Exp. No.	Mass (mg)	Time (mt)	Temp. °C	Lot No.	Gas(ml) Total	NO	N_2O	O_2	N_2	NO_2/N_2H_2	Solid residue(mg.) Oxide	Nitrite	Nitrate	Ratios BaO/BaN_2O_3	$Ba(NO_2)_2/BaN_2O_3$
17	100.00	—	240	a	0.55	nil	0.40 (72.7)	nil	0.15	nil					
			240	a	3.9	,,	2.4 (61.5)	,,	1.5						
			400	b	1.4	,,	0.7 (50.0)	,,	0.7						
18	124.00		260	a	3.5	,,	2.1 (60.0)	,,	1.4						
			400	b	3.2	,,	2.0 (62.5)	,,	1.2						
19	150.00		260	a	4.4	,,	2.8 (63.6)	,,	1.6						
			400	b	4.1	,,	2.4 (58.5)	,,	1.7						
20	175.00		260	a	4.8	,,	3.3 (68.7)	,,	1.5						
			400	b	4.1	,,	2.0 (48.9)	,,	2.1						
21	50.7	abrupt decomp.	450	—	2.5	,,	0.7 (28.0)	0.2	1.6	nil	7.2	30.4	7.5	0.15	0.65
22	100.00	,,	450	—	4.85	,,	1.45 (30.0)	0.2	3.2		13.8	63.1	7.7	0.15	0.70
23	172	—	550	b	4.5	,,	0.1 (2.0)	0.2 (4.0)	4.2 (94.0)						
			550	b	2.9	0.2 (6.6)	0.1 (3.3)	nil	2.6 (90.1)						

the production of hyponitrite as in(III) since it will stabilize the oxy-salt, so production of nitrogen will abate after the start of the reaction, it will again abate about the end, as found, when the quantity of oxy-salt is very low.

Taking the instance of the barium salt the reactions may be represented as follows—

(*a*) Decomposition as—

$$BaN_2O_3 \rightarrow BaO_2 + N_2O$$
$$BaN_2O_3 + BaO_2 \rightarrow Ba(NO_2)_2 + BaO$$
$$\overline{2BaN_2O_3 \rightarrow Ba(NO_2)_2 + BaO + N_2O}$$

accompanied by

(b) Disproportionation as—

$$2BaN_2O_3 \rightarrow BaN_2O_2 + Ba(NO_2)_2$$
$$\downarrow$$
$$BaO_2 + N_2$$
$$BaN_2O_3 + BaO_2 \rightarrow Ba(NO_2)_2 + BaO$$
$$\overline{3BaN_2O_3 \rightarrow 2Ba(NO_2)_2 + BaO + N_2}$$

Theory ratio (*a*) $BaO/2BaN_2O_3$ is 0.355, (*b*) $Ba(NO_2)_2/2BaN_2O_3$ is 0.503. Values for these, found in this work, are 0.302 and 0.55 respectively. Note that disproportionation which occurs tends to reduce (*a*) and increase (*b*) also that nitrate is always produced: this too affects the amounts of oxide and nitrate as a overall equations shown below—

$$6BaN_2O_3 \rightarrow 3Ba(NO_2)_2 + 3BaN_2O_2$$
$$\downarrow$$
$$3BaO_2 + 3N_2$$
$$BaN_2O_3 + 3BaO_2 \rightarrow Ba(NO_3)_2 + 3BaO$$
$$\overline{7BaN_2O_3 \rightarrow 3Ba(NO_2)_2 + Ba(NO_3)_2 + 3BaO + 3N_2}$$

The observation that nitrate is produced even when nitrogen(II)oxide—presumably oxygen carrier in sush reactions—is altogether absent supports intermediate peroxide formation theory.

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Electrometric Study on Cu(II), Hg(II) and Ag(I) Complexes of Isopropylmercaptan and Determination of their Solubility Products

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The complexation of copper (Cu^{+2}), mercury (Hg^{+2}) and silver (Ag^{+}) ion with isopropylmercaptan has been studied in 25% (V/V) ethanolic media employing potentiometric, conductometric and amperometric titration techniques. Copper and mercury ions from 1 : 2 complex while silver ion shows the formation of 1 : 1 complex. Equilibrium constants and solubility products of these complexes have been evaluated by Ringbom's method at 10°, 20° and 30°. The overall changes in thermodynamic functions ΔG, ΔH and ΔS accompanying complexation have also been determined at 20° with the help of an isobar and Gibb's Helmholtz equation.

THIOLS containing -SH group, have a tendency to form complexes with metals. Several metal complexes of thiols have already been studied by Saxena and co-workers[1-3], which have important applications in various disciplines like pharmaceutical, tanning and resin industries. The present communication reports the composition of sparingly soluble complexes of Cu(II), Hg(II), Ag(I) ions with isopropylmercaptan by amperometric, conductometric, potentiometric methods and determination of their equilibrium constants and solubility products at different temperatures.

Experimental

Isopropylmercaptan [$(CH_3)_2CH.SH$, referred herein as ISH] and other chemicals used were of AnalaR (B.D.H.) grade. Freshly prepared solutions were used to avoid the effects of ageing and air-oxidation.

Potentiometric and conductometric titrations, both direct and reverse, were performed in an inert atmosphere of Nitrogen using a Cambridge bench *p*H-meter and an electronic eye type conductometer. In both the direct titrations, title metal ions had the concentration $4\times10^{-3}M$ and were titrated against $0.1M$ ISH while in the reverse titrations $2\times10^{-3}M$ ISH and $4\times10^{-3}M$ ISH titrated against $5\times10^{-2}M$ title metal ions in the potentiometric and conductometric titrations, respectively. 25 ml of the titre solution in 25% (V/V) ethanol was used in each case and the end-points corresponding to the complex formation were obtained from the breaks in the titration curves.

Amperometric titrations were performed in an inert atmosphere of nitrogen using a manual polarograph with a scalamp galvanometer as current recorder and S.C.E. as reference electrode. The capillary used had the following characteristics in 25% (V/V) ethanol, $0.2M$ $NaClO_4$ and 0.002% Triton-X-100 at -0.7V vs S.C.E. with h_{eff} value being 38.1 cm., m = 1.390 mg/sec., t = 4.3 sec./drop. 25 ml solution of the titre in 25% ethanol contained $3\times10^{-3}M$ metal ion, $0.2M$ $NaClO_4$ and 0.002% Triton-X-100 and the concentration of the titrant used was $5\times10^{-2}M$ ISH in ethanol.

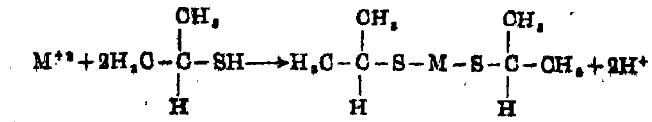
Results and Discussion

As reported earlier[4], isopropylmercaptan produces a diffusion controlled anodic wave associated with a pre-wave at d.m.e. It is observed that at -0.7V vs S.C.E., the metals under investigation are reducible but ISH shows inert behaviour. Hence amperometric titrations at -0.7V were carried out in 25% ethanol, $0.2M$ $NaClO_4$ and 0.002% Triton-X-100 for determining the composition, equilibrium constants and solubility products of the complexes at different temperatures.

Stoichiometry :

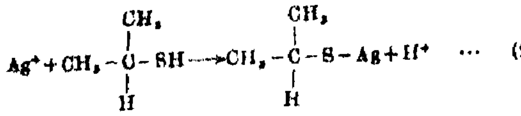
For establishing the stoichiometry of the complex species formed during the interaction of metal ion and ISH, a series of conductometric, potentiometric and amperometric titrations were carried out using different concentration of reactants both by direct and reverse methods (Fig. 1). The equivalence points in the titrations curves corresponded to the formation of 1 : 2 complex for Cu(II), Hg(II) and 1 : 1 for Ag(I) in accordance with the following equations.

For 1 : 2 complex :



(where M^{+2} stands for Cu^{+2}, Hg^{+2}) ... (1)

For 1 : 1 complex :


... (2)

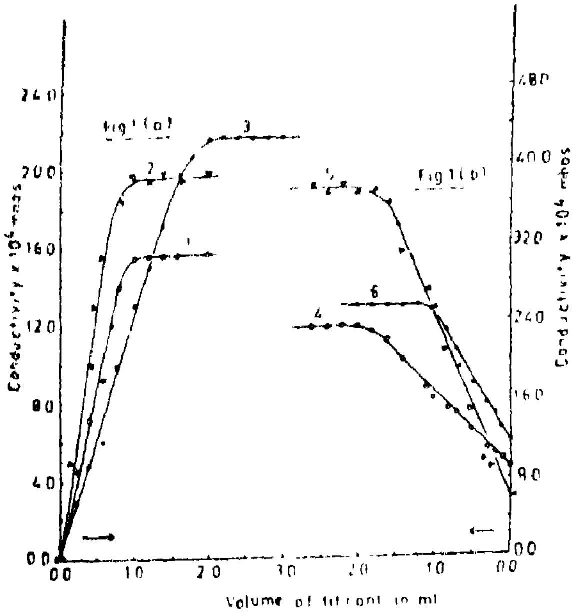


Fig. 1(a) Curves 1, 2, 3—conductometric titrations of 25 ml solutions containing $4\times10^{-3}M$ ISH against (M/20) Cu^{+2}, Hg^{+2}, Ag^{+} (metal nitrates) respectively.

Fig. 1(b) Curves 4, 5, 6—conductometric titrations of 25 ml. solution containing $4\times10^{-3}M$, Cu^{+2}, Hg^{+2}, Ag^{+} respectively against 0.1*M* ISH.

Equilibrium constants and solubility products : The values of equilibrium constants for the complexation reactions between metal ion and the ligand have been determined by Ringbom's method[5]. The following equation[6] has been used for evaluating K_t, the conditional or formal equilibrium constant.

$$\frac{(i-i_r)(1+rf)}{(i_0-i_r)} = \frac{(1-f)+[(1-f)^2+4(1+rf)^2/K_t(C_M^0)^2]^{\frac{1}{2}}}{2} \quad \dots (3)$$

where *r* is the dilution parameter $(r=C_M^0/C_x)$ and *f* is the titration parameter defined by the equation

$$f=Z.\frac{V_x C_x}{V_M^0 C_M^0} \quad \dots (4)$$

Z being the number of moles of the titre which react with each mole of the titrant ; in the present case Z=0·5 for Cu(II), Hg(II) and 1 for Ag(I). C_M^0 and i_0 are the initial concentration and limiting current of the metal ion respectively ; i_r and i are respectively the residual current and the current at any titration point. The titration parameter f becomes equal to unity at the equivalence point.

When a *reducible ion is titrated* with an inert one to give a precipitate, equation(3) at the equivalence point can be written as

$$K_t=\left(\frac{1}{C_M^0}\times\frac{i_0-i_r}{i-i_r}\right)^2 \quad \dots (5)$$

from which the value of K_t under the experimental conditions of the titration can be obtained. The value of the $\frac{i_0-i_r}{i-i_r}$ at the equivalence point was obtained from the plot of $\frac{i-i_r}{i_0-i_r}\times\frac{V_0+v}{V_0}$ vs f (Fig. 2.). $\frac{V_0+v}{V_0}$ is the volume correction factor at any titration point.

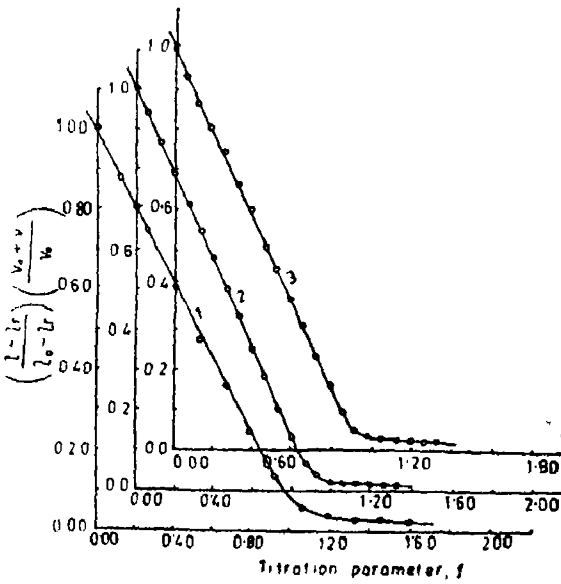


Fig. 2 Curves 1, 2, 3—plot fo $\frac{i-i_r}{i_0-i_0}\times\frac{V_0+v}{V_0}$ vs f for Ag^+, Hg^{+2}, Cu^{+2} respectively at 10°.

TABLE 1—VALUES OF K_t AND K_s FOR Cu(II), Hg(II) AND Ag(I) COMPLEXES OF ISOPROPYLMERCAPTAN AT DIFFERENT TEMPERATURES

Complex	Equilibrium constant (K_t)			Solubility product (K_s)		
	10°	20°	30°	10°	20°	30°
Cu(II)	12.35×10^7	3.67×10^7	1.98×10^7	8.18×10^{-9}	27.28×10^{-9}	50.68×10^{-9}
Hg(II)	27.44×10^7	6.95×10^7	4.45×10^7	3.60×10^{-9}	14.40×10^{-9}	22.49×10^{-9}
Ag(I)	15.37×10^6	11.11×10^6	7.11×10^6	6.51×10^{-8}	9.01×10^{-8}	14.06×10^{-8}

In the absence of any side reaction that could consume either ion, K_t for the precipitation titration is the reciprocal of the solubility product. Thus solubility products, K_s for Cu(II), Hg(II) and Ag(I) complexes may also be evaluated and values of K_t and K_s for different complexes of ISH at three different temperatures are given in Table 1.

Thermodynamic functions : The values of changes in the free energy($\triangle G$), enthalpy($\triangle H$) and entropy($\triangle S$), accompanying the complexation reactions have been determined at 20° with the help of standard equations[7]. The value of $\triangle G$ is obtained from the expression $\triangle G = -RT \ln K_t$, where K_t is the equilibrium constant. $\triangle H$ is determined with the help of an isobar $\frac{d \ln K_t}{dt} = \frac{\triangle H}{RT^2}$ which may be written as $\frac{d \log K_t}{d(1/T)} = -\frac{\triangle H}{4.57}$. The values of $\log K_t$ obtained at different temperatures are plotted as a function of 1/T. The gradient of the tangent drawn at the point corresponding to 20° is determined and equated to $-\frac{\triangle H}{4.57}$. $\triangle S$ is then evaluated from the relation $\triangle S = \frac{\triangle H - \triangle G}{T}$

The values of $\triangle G$, $\triangle H$ and $\triangle S$ are summarised in Table 2.

TABLE—2 THERMODYNAMIC FUNCTIONS FOR Cu(II), Hg(II) AND Ag(I) COMPLEXES OF ISOPROPYLMERCAPTAN AT 20°

Metal Complex	$\triangle G$ (K cal/mole)	$\triangle H$ (K cal/mole)	$\triangle S$ (cal/deg/mole)
Cu(II)	−10.14	−19.71	−12.18
Hg(II)	−10.52	−13.41	− 9.85
Ag(I)	− 9.45	− 6.74	+ 9.25

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Polarographic Studies on Nickel(II), Copper(II) and Zinc(II) Complexes of 3-Hydroxypyridine-2-Thiol

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Polarographic reduction of Nickel(II), Copper(II) and Zinc(II) in presence of 3-hydroxypyridine-2-thiol has been studied. Diffusion controlled irreversible waves are obtained in all cases. Kinetic parameters, viz., transfer coefficient (α) and formal rate constant $\left(K^{0}_{f,h}\right)$ have been evaluated. The order of stability of the complexes have been found to be $Cu^{2+} > Zn^{2+} > Ni^{2+}$.

SULPHUR atom either as a thiol, a thioether or a sulphide ion is an important ligand in certain biological systems. Polarographic investigations on the metal complexes of sulphur donor ligands, therefore, warrant attention. The present paper describes the results of polarographic investigations on Nickel(II), Copper(II) and Zinc(II) complexes of *3-hydroxypyridine-2-thiol* (HPT), a potential sulphur donor ligand. Kinetic parameters have been evaluated and order of the stability of the complexes has been discussed.

Polarographic studies on Nickel(II)[1-4], Copper(II)[5-8] and Zinc(II)[7-11] complexes with Sulphur donor ligands have not received due attention.

Experimental

Polarograms were obtained on a manual polarograph recommended by Kolthoff. Current was measured on a galvanometer (General Electric Co., USA) which was standardised by passing a known current. The potential was measured by a Leeds Northrup students potentiometer standardised against a standard cadmium cell. All the potentials are expressed versus S.C.E. The capillary used had the following characteristics: $m^{2/3}t^{1/6} = 2.054$ $mg^{2/3}\ sec^{-\frac{1}{2}}$ $h = 40$ cms and $t = 3.8$ seconds. All studies were made at room temperature (30±0.1°).

Materials: Stock solutions of metal ions were prepared by dissolving A.R. grade salts in double distilled water. Solution of HPT (Fluka AG, Switzerland) was prepared in purified methanol due to its limited solubility in water.

Reagent grade chemicals were used for preparing buffers and electrolyte solution.

Technique: A series of solutions containing 1×10^{-4} *M* metal ion, appropriate amounts of supporting electrolyte, buffer, maximum suppressor (gelatin) and varying amounts of HPT were polarographed. The medium was 40% methanol. A fixed minimum distance was maintained between the electrodes and it was checked that the cell resistance did not exceed 1000 ohms. The solutions were previously deaereated by passing nitrogen, which was purified by bubbling through vanadous sulphate solution. A slow stream of nitrogen was maintained above the solution surface while recording polarograms.

Results and Discussions

Well defined single reduction waves are obtained in all cases. Studies with different heights of mercury column reveal constant value for $i_d/(h_{eff})^{\frac{1}{2}}$ indicating the diffusion controlled nature of the waves. Diffusion current, i_d, increases linearly with increase in metal ion concentration under similar experimental conditions. With increase in ligand concentration, $E_{\frac{1}{2}}$ shifts towards negative value indicating complex formation. The values of i_d fall in the range of two electron reduction. The plots of $-E_{d.e}$ *vs.* log $(i/i_d\text{-}i)$ is linear for each system. Slopes of these lines are higher than the theoretical value of 2.303RT/nF indicating the irreversible nature of the waves. For the evaluation of the rate constant of the electrode reduction proper, the method developed by Koryta[12-14], imposes an ambiguity in the gross assumptions that the increasing concentration of the ligand does not change the structure of electrode double layer. The heterogeneous rate constant for the overall cathodic process has been determined, therefore, by the modified method of Oldham and Parry[15].

According to these authors the equation for an irreversible diffusion controlled wave is

$$-E_{d.e} = -E_{\frac{1}{2}} + \frac{2.303\ RT}{nF} \log \left[\frac{x(5.5-x)}{15(1-x)}\right] \quad \dots \quad (1)$$

where $x = \frac{i_E}{i_{lim}}$ (i_E = current at potential E) which is valid in the entire region $0 \leqslant x \leqslant 1$. From the plot of $-E_{d.e.}$ vs. $\log\left[\frac{x(5.5-x)}{5(1-x)}\right]$, the values of $\frac{2.303\,RT}{nF}$ and $E_{\frac{1}{2}}$ can be evaluated from the slope and intercept respectively. Also for an irreversible wave the half-wave potential is related to the rate constant for the electrode reduction (at 30°) by the equation.

$$E_{\frac{1}{2}} = E_0 + \frac{2.303\,RT}{nF} \log 0.89\, k^{0}_{f,h} \sqrt{\frac{t}{D}} \quad \ldots \quad (2)$$

where $k^{0}_{f,h}$ is the formal rate constant at an arbitrary chosen reference potential E_o, ($E_o = 0.0$ vs. NHE or -0.2412 vs. SCE) and D and t have their usual meaning. Values of kinetic parameters have been presented in Table 1.

TABLE—1 KINETIC PARAMETERS

Ligand concn. (mM)	$-E_{\frac{1}{2}}$ (volts vs. SCE)	αn	$D^{\frac{1}{2}} \times 10^3$ (cm.sec.$^{-\frac{1}{2}}$)	$k^{0}_{f,h}$ (cm.sec.$^{-1}$)	$\alpha.\Delta E_{\frac{1}{2}}$ (volts)
Ni(II) – HPT, pH = 9.7(NH_4Cl/NH_4OH Buffer) μ = 0.1(KNO_3)					
2.0	1.280	0.940	1.86	0.062×10^{-19}	0.085
4.0	1.300	0.935	1.84	0.037×10^{-19}	0.093
6.0	1.316	0.936	1.80	0.019×10^{-19}	0.101
8.0	1.324	0.935	1.80	0.015×10^{-19}	0.106
Cu(II) – HPT, pH = 10.0(OH^-/PO_4^{3-} Buffer), μ = 0.1(KNO_3)					
2.0	0.320	0.855	2.08	0.99×10^{-4}	0.137
4.0	0.340	0.850	2.06	0.52×10^{-4}	0.145
6.0	0.355	0.849	2.03	0.31×10^{-4}	0.151
8.0	0.362	0.847	2.01	0.25×10^{-4}	0.153
Zn(II) – HPT, pH = 10.0 (OH^-/PO_4^{3-} Buffer), μ = 0.1 (KCl)					
2.0	1.258	1.096	2.10	0.035×10^{-20}	0.115
4.0	1.273	1.086	2.08	0.030×10^{-20}	0.122
6.0	1.283	1.080	2.09	0.027×10^{-20}	0.126
8.0	1.286	1.074	2.04	0.019×10^{-20}	0.128

A perusal of results shows that irreversibility of the chelates is increasing in the order $Zn^{2+} > Ni^{2+} > Cu^{2+}$.

Since the increase in the concentration of the complexing agent does not cause any drastic change either in the shape or in the position of the reduction waves, it may be inferred that the mechanism of the electrode processes remains same throughout the concentration range and the main parameter which is influenced by the change in the composition of the solution is $E_{\frac{1}{2}}$. Since the stability of the complexes is reflected in the change in half-wave potential from simple metal ion to the complexed metal ion, a comparison of $E_{\frac{1}{2}}$ values may give an idea about the relative stabilities of the complexes of the metal ions under study. But in the case of irreversible processes, the half-wave potential also depends upon α and, hence, the $E_{\frac{1}{2}}$ values corresponding only to the same value of α may be compared. However, Vlček[15] suggests that this difficulty may be overcome if the values of $\alpha E_{\frac{1}{2}}$, instead of those of $E_{\frac{1}{2}}$, are used. The values of $\alpha \Delta E_{\frac{1}{2}}$ are listed in Table 1. The results show that the stability of the complexes follows the order, $Cu^{2+} > Zn^{2+} > Ni^{2+}$. This order is different from the common order of Irwing and Williams[16] and Mellor and Malley[17] only in that the positions of Zn^{2+} and Ni^{2+} are reversed. Murakama *et al*[18] suggest that the greater stability of Zn^{2+} complexes may be due to the fact that besides L→M σ-bond there is some M→L π-interaction between the dπ orbitals of the metal ion and π-orbitals of the ligand molecule. Extent of such π-interaction with Zn^{2+} is greater than with Ni^{2+}.

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Proton-Ligand Stability Constants of some Amino Acids**

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Proton-ligand stability constant of hippuric acid as also of glycine, ∝ and β-alanine determined by the method of Irving-Rossotti in 50% V/V ethanol-water mixture at 30° and 0.1 ionic-strength have been reported. The log K_1^H and log K_2^H values for the three amino acids have also been reinvestigated in water medium under similar conditions. The differences of stability constant values in the mixed solvent and water are fairly positive in case of log K_2^H (for carboxylic proton) and slightly negative in case of log K_1^H, as expected. In case of β-alanine, log K_2^H value is higher than that of the ∝-isomer due to the increased distance of the amino and the carboxylic groups. The pK* value for hippuric acid as computed by half-integral and graphical method has been found to be 4.3 at 30° and 0.1 ionic strength.

In dicumarol and other anticoagulant therapy using rare-earth salts for thrombotic diseases, hippuric acid test is utilised as a diagonistic tool for testing liver-function and its capacity to synthesize some of the blood-coagulant factors[1]. In order to study the metal-binding capacity, particularly of some biologically active metal ions by hippuric acid, benzoyl glycine, we have undertaken some studies of the nature of dissociation of hippuric acid. In our present paper we have reported the proton-ligand stability constant of hippuric acid using *p*H-titration technique of Bjerrun-Calvin as modified by Irving-Rossotti[2] in 50% V/V ethanol-water mixture as the compound is only sparingly soluble in water. Although values of log K_1^H and log K_2^H for different amino acids have been worked out by various authors through different techniques and are available in standard literature[3], the data for glycine, ∝- and β-alanine under same conditions have been parallely presented in the present communication with a view to having a comparative and correlative idea of the protonation of hippuric acid by the same technique.

Experimental

Materials : Double-distilled water was used. Ethanol was purified before use by the standard method[4]. Perchloric acid used was of AR grade (E. M. Company). Carbonate-free alkali solution was prepared using AR grade sodium hydroxide pellets. Perchloric acid and sodium hydroxide solutions were standardised potentiometrically against standard solution of potassium-hydrogen-phthalate.

The amino acids were of AR grade and their purity was tested by the method of formol-titration[5]. Their solutions were prepared in 50% V/V ethanol-water mixture. Sodium perchlorate (pure) solution used to maintain constant ionic strength was standardised by estimating the perchloric acid obtained after passing the solution through Amberlite IR-120(H-form) resin.

Procedure : *p*H-titrations were performed with two sets of solutions ; (i) Perchloric acid+sodium perchlorate ; (ii) Perchloric acid+amino acid+sodium perchlorate, the total volume being 50 ml in each set. Constant ionic strength of 0.1 was maintained by adding required volume of sodium perchlorate solution. The final concentration of Perchloric acid and amino acids were $3.2\times10^{-2}M$ and $2.0\times10^{-2}M$ respectively. The alkali used was 0.58*M*.

Measurements were done at 30°±0.5 using Beckman glass-electrode of 0-14 *p*H range in conjunction with SCE connected by means of an agar-2*M* sodium nitrate bridge.[6]

From the titration curves of free acid and (free acid+amino acid), the average number of protons associated with amino acids ($\bar{n}_A$) were calculated using the formula of Irving-Rossotti[2] :—

$$\bar{n}_A = y - \frac{(v''-v')(N^\circ+E^\circ)}{(V^\circ+v')TC^\circ_L} \quad \ldots (1)$$

where v′ & v″ are the volumes of alkali required to reach the same *p*H in free acid and free acid+amino acid titration curves respectively, N°, E° and TC°_L are the initial concentrations of alkali, perchloric acid and amino acids respectively, y is the number of dissociable protons in amino acids, V° is the initial volume of the solutions.

The formation curves were drawn by plotting the $\bar{n}_A$ values against their corresponding *p*H and

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the stability constants were determined by half-integral method. The acid dissociation constant (pK*) of hippuric acid has also been computed by graphical method using the formula.

$$pH = \log \frac{1-\bar{n}_A}{\bar{n}_A} + pK^* \qquad \dots \quad (2)$$

Results and Discussion

With a view to extending the method of Irving-Rossotti in case of amino acids and obtaining the log K_2^H value of the carboxylic proton in lower pH-region, we have used more than one equimolecular amounts of perchloric acid compared to amino acids so that the amino acids exist as $\overset{+}{N}H_3RCOOH$ form. In such condition, the pH values of the initial solutions have been higher than the free strong acid because of the protonation of the basic $-COO^-$ group, and the dipolar ion has been converted to the acid form, $\overset{+}{N}H_3RCOOH$. This trend is observed till the acid form has completely been converted into the dipolar ion $\overset{+}{N}H_3RCOO^-$ (Figs. 1 & 2). In this region of the titration curves, ($v'>v''$ and we have calculated $\bar{n}_A$ by rearranging the equation (1) which comes out as :

$$\bar{n}_A = y + \frac{(v'-v'')(N^\circ+E^\circ)}{(V^\circ+v')TC^\circ_L}$$

In higher pH regions, values of $\bar{n}_A<1$ are obtained

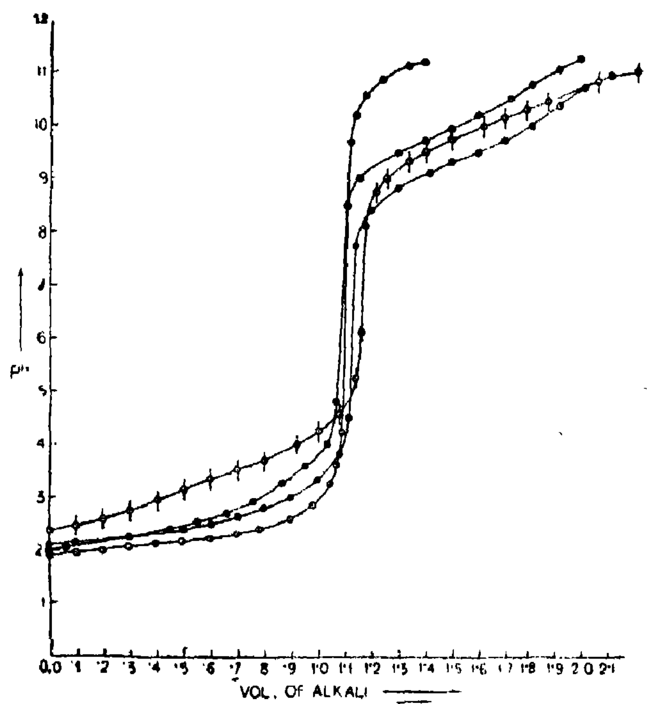


Fig. 1 Titration curves of amino acids in water medium

-⊙- : Strong acid
-⊗- : Strong acid + glycine
-●- : Strong acid + α-alanine
-⊙- : Strong acid + β-alanine.

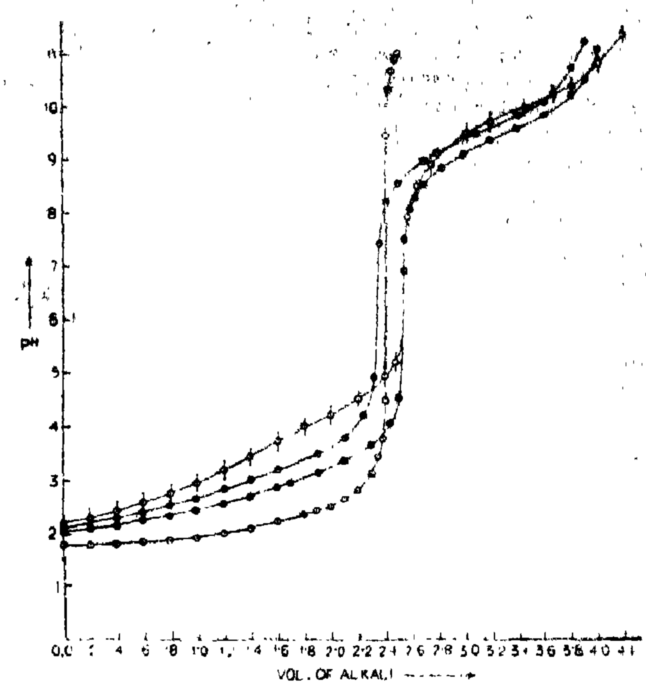
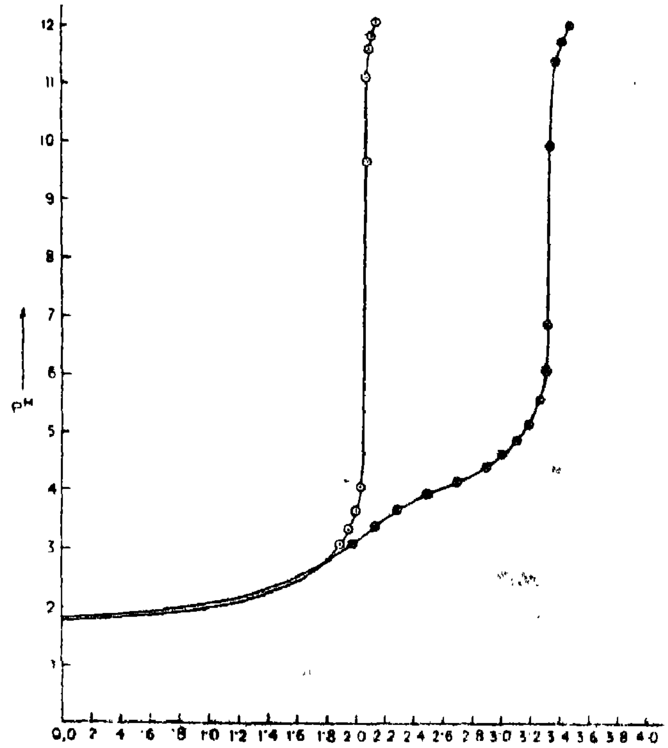


Fig. 2 Titration curves of amino acids in 50% V/V ethanol-water medium.

-○- : Strong acid
-⊗- : Strong acid + glycine
-●- : Strong acid + α-alanine
⊙ : Strong acid + β-alanine.



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Fig. 3 Titration curve of hippuric acid and strong acid in 50% V/V ethanol-water medium.

-⊙- : Strong acid
-⊗- : Strong acid + hippuric acid.

by the use of equation (1) where $v'' > v'$. The $\bar{n}_A$ values thus obtained extends over a range $0.2 < \bar{n}_A < 2.0$ and are plotted against pH values (Figs. 4 & 5) wherefrom the log H_1^H and log K_2^H are determined by the method of half-integral at the points $\bar{n}_A = 0.5$ and 1.5 respectively.

From the formation curves of amino acids in water and in ethanol-water mediums, it can be seen that log K_2^H values are markedly increased in ethanol-water medium than those in water medium (Figs. 4 & 5) due to the lowering of dielectric constant of the mixed solvent where the dissociation of proton is negatively favoured and thereby giving higher stability-constant values (Table 1). On the other hand, there is no such marked change in log K_1^H values as the role of dielectric constant of the mixed-solvent is less effective in comparison with much increased OH^- concentration of the system, at the higher pH-region. Our observation is consistent with the earlier observations on the nature of such variations in mixed-solvent of different composition[7,8].

TABLE—1

(Temp = 30° ± 0.5 ; μ = 0.1)

	log K_1^H		log K_2^H	
	Water	50% V/V ethanol-water	Water	50% V/V ethanol-water
Glycine	9.75	9.25	2.25	2.75
α-alanine	9.85	9.50	2.30	3.15
β-alanine	9.7	9.55	3.60	3.95
Hippuric acid	—	—	—	4.3(a) 4.3(b)

(a) by the method of half-integral
(b) pK* determined by graphical method.

The log K_2^H values of α- and β-alanine respectively are 3.15 and 3.95 in 50% V/V ethanol-water and 2.3 and 3.6 in water (Table 1). The higher value in the case of β-isomer is due obviously to the less-effective influence of β-amino group on the dissociation of the carboxylic proton, as a result of the increased distance of the two poles. Such a role of distance on the dissociation has, however, been observed in case of long-chain amino acids like ω-amino acids[9].

Thomas & Niemany[10] indicated from cryoscopic studies that there is a small but significant amount of diprotonation of the amino acids in absolute sulphuric acid. From Figs. 4 & 5, it can be seen that the values of $\bar{n}_A$ reached to about 2 at a pH near 2. These values indicate that the acid form of the amino acids, $\overset{+}{N}H_3RCOOH$, can still take up proton in perchloric acid medium, at such a low pH, and diprotonation is a possibility, in accordance with the following reaction :

$$\overset{+}{N}H_3RCOOH + HClO_4 \rightleftharpoons \overset{+}{N}H_3RCOOH_2^+ + ClO_4^-$$

In the case of titration of hippuric acid, the titration curve of perchloric acid + hippuric acid and that of perchloric alone practically coincide (Fig. 3) up to pH until the strong acid is fully neutralised. The carboxylic group of the hippuric acid do not form the conjugate base $-COO^-$ intramolecularly indicating practically the absence of any dipolar

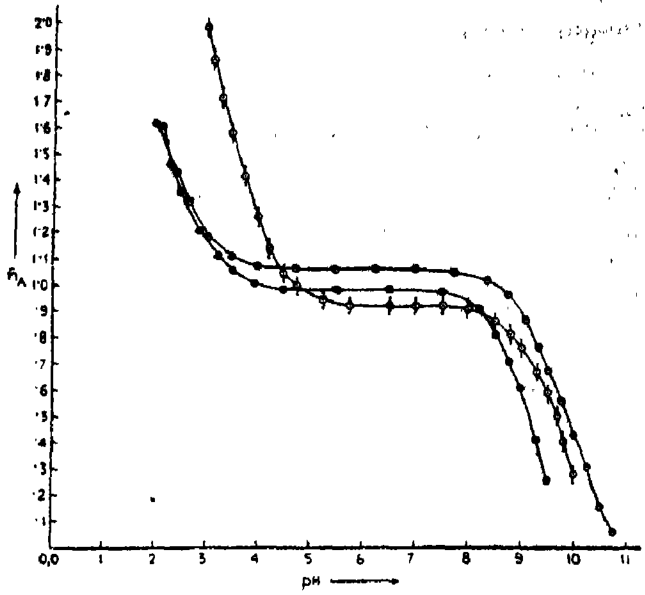


Fig. 4 Formation curves of amino acids in water medium.
-⊗- : Glycine
-●- : α-alanine
○ : β-alanine.

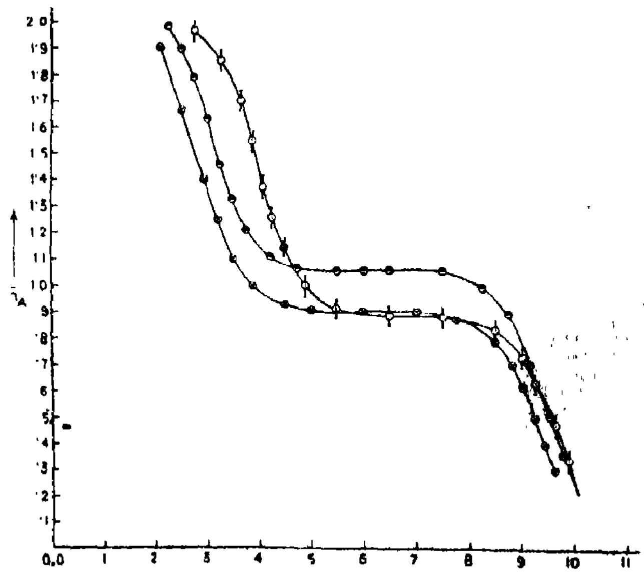


Fig. 5 Formation curves of amino acids in 50% V/V ethanol-water medium.
-⊗- : Glycine
-●- : α-alanine
○ : β-alanine

form. There is only one inflection in the combined strong acid hippuric acid curve (Fig. 3) indicating the dissociation of only of the carboxylic proton.

The $\bar{n}_A$ values for hippuric acid are calculated from the titration curves by equation (1) and are plotted against pH when log K^H determined by half-integral method at the point $\bar{n}_A = 0.5$ has been found to be 4.3 (Fig. 6). The graphical method is also applied to calculate pK* by equation (2) where $\log \frac{1-\bar{n}_A}{\bar{n}_A}$ are plotted against pH and pK* determined from the intercept of the straight line is 4,3 (Fig. 6).

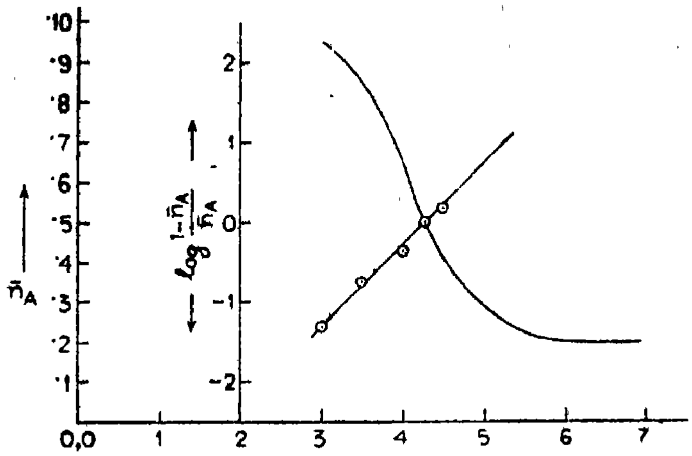


Fig. 6 Formation curves of hippuric acid.

- : Half-integral method

-○- : Graphical method.

From the curve, it is thus evident that there is but slight probability of the hippuric acid to exist in a form like $C_6H_5CO\overset{+}{N}H_2CH_2COO^-$ as the benzoyl group withdrawing electron-density from around the nitrogen, reduces its electron-pair-donar-capacity and accordingly protonation of −NH-group is expected least.

The pK* value of hippuric acid reported in the present communication is evidently less than the pK value of acetic acid (pK=4.76). This small increase in dissociation may, however, be due to the presence of −NH-group which has the capacity, even to a little extent, to pull proton from the carboxyl group, a phenomenon absent in the case of acetic acid. On the other hand, pK value of acetyl glycine which is much raised than that of glycine, i.e., from 2.75 for glycine (in 50% V/V ethanol-water) to 3.7 for acetyl glycine[8,11] due to the electron-withdrawing tendency of the acetyl group. Phenyl group being more electron-withdrawing, (enhances the electron-withdrawing) capacity of C_6H_5CO-group. Thus the proton-ligand stability value of hippuric acid is increased than that of acetyl glycine as evidenced from the pK* value of 4.3 for benzoyl glycine reported by us.

From the data presented in this paper for glycine and hippuric acid in 50% V/V ethanol-water medium (Table 1) and from the standard dissociation constant values for acetyl glycine and acetic acid, the proton-ligand stability constants (for carboxylic proton) may be arranged, as expected in the following order :

Glycine < acetyl glycine < benzoyl glycine < acetic acid

2.75* < 3.7 < 4.3* < 4.76

* (in 50% V/V ethanol-water)

Acknowledgement

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Kinetics and Mechanism of the Silver(I) Ion Catalysed Oxidation of Propionic Acid by Peroxodisulphate Ion

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Kinetics of Ag(I)-catalysed oxidation of propionic acid by peroxodisulphate have been studied. The rate is first order in peroxodisulphate and silver(I). A complex formation between Ag^+ and propionic acid (P. A.) is indicated. The following rate law holds :

$$-\frac{d[S_2O_8^{2-}]}{dt} = [S_2O_8^{2-}]\left\{k_1 + \frac{k_2[Ag^+]_T}{(1+K[PA])}\right\}$$

The values of k_1 and k_2 were found to be 0.30×10^{-4} sec^{-1} and 0.21 M^{-1} sec^{-1} respectively at 60°.

PEROXODISULPHATE oxidations of several organic and inorganic substrates both under catalysed and uncatalysed conditions have been a field of interest for several group of workers[1-3]. Among the monocarboxylic acids, oxidations of formate[3] and the acetate[4] ions by peroxodisulphate have been studied, but the oxidation of propionic acid remains uninvestigated.

Experimental

Potassium peroxodisulphate, silver sulphate, propionic acid and other chemicals (E.Merck, G.R.) were always prepared fresh in doubly distilled water and standardized by usual methods.

A kinetic run was initiated by adding the required volume of peroxodisulphate solution into the reaction vessel containing the requisite amounts of propionic acid and silver sulphate solutions kept at a desired temperature in a thermostat within ±0.1°. The progress of the reaction was studied by estimating residual peroxodisulphate iodometrically[5] at different intervals of time.

Results

Stoichiometry and Reaction products :

The stoichiometry of the reaction was determined with known excess of potassium peroxodisulphate (0.04 *M*) over propionic acid at two different concentrations (0.002 *M* and 0.004 *M*) under identical conditions. The excess peroxodisulphate was determined iodometrically[5]. It was found that two moles of peroxodisulphate are consumed per mole of the acid.

The main reaction products were acetaldehyde and carbon dioxide. Acetaldehyde was identified in the reaction mixture by spot test[6] and its conversion into 2 : 4-dinitrophenyl hydrazone derivative which was subsequently identified by its m.p.

Rate Measurements :

Preliminary experiments showed that the reaction proceeds with a measurable rate above 50° with 0.02*M* reactant concentrations and $2 \times 10^{-4} M$ Ag^+ concentration. Peroxodisulphate follows a first order disappearance at all the concentrations. Hence the values of 'k' given in the following tables have been obtained from the slopes of the linear first order plots between log [a-x] vs. time.

(a) Peroxodisulphate dependence :

The variation of the rate over a ten fold range of initial $S_2O_8^{2-}$ concentrations was studied. The values of the rate constants obtained from the first-order linear plots at different $S_2O_8^{2-}$ concentrations are tabulated below :

TABLE—1 PEROXODISULPHATE DEPENDENCE

[Propionic acid] = 0.02*M*, $[Ag_2SO_4] = 2 \times 10^{-4} M$, Temperature = 60°

$[S_2O_8^{2-}] \times 10^2 M$ =	0.5	1	2	3	4	5
$k \times 10^4$ sec.$^{-1}$ =	1.19	1.17	1.15	1.17	1.28	1.28

Evidently, the order of the reaction which respect to peroxodisulphate is one.

(b) Propionic acid dependence :

The rate constants corresponding to different initial concentrations of propionic acid are summarized in Table 2.

TABLE—2 PROPIONIC ACID DEPENDENCE

[Potassium peroxodisulphate] = 0.02*M*, $[Ag_2SO_4] = 2 \times 10^{-4} M$, Temp. = 60°

[Propionic acid] $\times 10^2 M$ =	0.5	1	2	3	4	5
$k \times 10^4$ sec^{-1} =	1.40	1.36	1.15	1.02	1.02	0.98

Table 2 shows that the rate constants tend to decreas with increasing concentrations of propionic acid. It appears that the rate is indepen dent of the concentration of propionic acid and the decreasing trend of the rate constants may be ascribed to a decrease of concentration of Ag(I) owing to a complex formation of Ag(I) and propionic acid.

(c) Silver ion concentration dependence :

The Ag(I) coneentration was varied in the range $(2\text{-}10)\times10^{-4}M$ and the results are given in Table 3.

TABLE—3 SILVER(I) DEPENDENCE

[Potassium peroxodisulphate] = 0.02*M*, [Propionic acid] = 0.02*M*, Temperature = 60°

$[Ag^+]\times10^4 M$	= 2	4	6	8	10
$k\times10^4$ sec.$^{-1}$	= 0.75	1.15	1.62	1.92	2.41

Plot of k against silver ion concentration gives a linear relationship. Computation of the data of the above table shows that the observed rate constant satisfies the equation :

$$k = k' + k''[Ag^+]$$

where k' and k'' are the rate constants for the uncatalysed and catalysed pathways respectively with values 0.3×10^{-4} sec^{-1} and $0.21 M^{-1}$ sec^{-1}, obtained from the intercept and slope of the linear plot.

The decrease of the rate constant with the increase of propionic acid concentration could be due to a complex formation of Ag(I) and the organic acid. This necessiated further investigations. Evidence for the adduct formation of propionic acid with Ag(I) was obtained from the rate constant – Ag(I) concentration plots obtained with varying concentrations of propionic acid at different concentrations of Ag(I). The rate data at three different acid concentrations (0.01*M*, 0.02*M*, 0.03 *M*) satisfy the equations :

$$k = 0.30\times10^{-4} + 0.25[Ag^+]\ \text{sec}^{-1} \quad \dots \quad (I)$$
$$k = 0.30\times10^{-4} + 0.21[Ag^+]\ \text{sec}^{-1} \quad \dots \quad (II)$$
$$k = 0.30\times10^{-4} + 0.18[Ag^+]\ \text{sec}^{-1} \quad \dots \quad (III)$$

In each case different values of k'' but the same value of k' is obtained.

The effect of hydrogen ion was studied by varying perchloric acid in the concentration range (0.01-0.06) *M* and there is almost no effect. Allyl acetate decreased the rate, but no limiting rate was obtained.

Mechanism :

The catalytic activity of silver ion is due to the formation of higher valent silver species. The nature of these species (Ag(II) and Ag(III)) has been discussed by Anderson and Kochi[7]. Recent evidences point to the existence of Ag(II) in aqueous acid solution which is in accordance with the observation of Higginson and Marshall[8].

The various rate dependences in the present reaction lead to the following mechanism :

$$S_2O_8^{2-} \xrightarrow{k_1} 2SO_4^{\cdot-} \quad \dots (1)$$

$$SO_4^{\cdot-} + P.A. \xrightarrow{fast} \text{products} \quad \dots (2)$$

$$Ag^+ + P.A. \overset{K}{\rightleftharpoons} \text{complex} \quad \dots (3)$$

$$S_2O_8^{2-} + Ag^+ \xrightarrow{k_2} 2SO_4^{2-} + Ag^{3+} \quad \dots (4)$$

$$Ag^{3+} + P.A. \xrightarrow{fast} \text{products} \quad \dots (5)$$

If Ag^+ and not the Ag^I complex is reactive, following rate law would be obtained :

$$-\frac{d[S_2O_8^{2-}]}{dt} = k_1[S_2O_8^{2-}] + k_2[S_2O_8^{2-}][Ag^+]_{free} \dots (6)$$

$$\text{or} \quad k = k_1 + k_2[Ag^+]_{free} \quad \dots (7)$$

$$= k_1 + \frac{k_2[Ag^+]_T}{(1+K[P.A.])} \quad \dots (8)$$

where $[Ag^+]_{free}$ and $[Ag^+]_T$ are the concentrations of free silver ion and total Ag(I). Equation (8) at constant P.A. would reduce to (9).

$$k = k_1 + k''[Ag^+]_T \quad \dots (9)$$

where k_1 is identical with k'. An average value of K was found to be 24 M^{-1}. The second order rate constant was calculated to be 0.21 M^{-1} sec^{-1}.

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A Study of the Dependence of the Slope S_v of the ϕ_v vs $\sqrt{C}$ Curves. Part III : Ethanol-Water Mixtures

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The effect of the dielectric constant of the medium on the nature (positive and negative) of the slope S_v of the apparent molar volume, ϕ, vs $\sqrt{C}$ curves of some tetraalkylammonium iodides has been examined in this communication using ethanol-water mixtures as mixtures of known but different dielectric constants. The negative slope for the Pr_4NI and Bu_4NI salts becomes positive around 64 and 58 dielectric constants respectively. These values are very close to those for dioxane-water and methanol-water systems. The results of these communications taken together seem to indicate the dominant role of the dielectric constant of the medium in controlling the nature of the slope.

In continuation with the earlier communications[1,2] from this laboratory, dealing with the effect of the dielectric constant of the medium on the slope S_v of the Masson's equation viz.,

$$\phi_v = \phi_o + S_v \sqrt{C}$$

ϕv and ϕo being the apparent molar volumes at dilution 'v' and at infinite dilution respectively, in the case of some tetraalkylammonium salts in dioxane-water[1] and methanol-water[2] mixtures, the studies have been extended to ethanol-water mixtures with a view to examine whether replacing dioxane and methanol by ethanol will have any significant effect on the slope. The dielectric constant of ethanol-water mixtures of different ethanol contents have been reported in the literature.[3] These mixtures have been used here as solvents of different dielectric constants.

Experimental

Absolute alcohol (≃99.5%) was obtained from double distilled rectified spirit in the usual manner. Further purification of absolute alcohol thus obtained was carried out as per procedure given below :

5 gms of magnesium turnings and 0.5 gm (approx.) of iodine were placed in a flask to which 75 ml of absolute alcohol were added. The flask was heated gently until all magnesium had dissolved. To this 900 ml more of absolute alcohol were added and the mixture was refluxed for 30 minutes. Alcohol was then distilled off and was taken to be 99.95% pure ethyl alcohol and was used with conductivity water for preparing mixtures of known dielectric constant[3]. Mixtures containing 9.67%, 19.86%, 34.47%, 42.15% and 54.23% by weight of alcohol, having respectively the dielectric constants at 25° as 72.99, 67.08, 58.37, 53.60 and 46.66 were prepared and were used for preparing solutions. Tetraalkylammonium iodides were purified in the

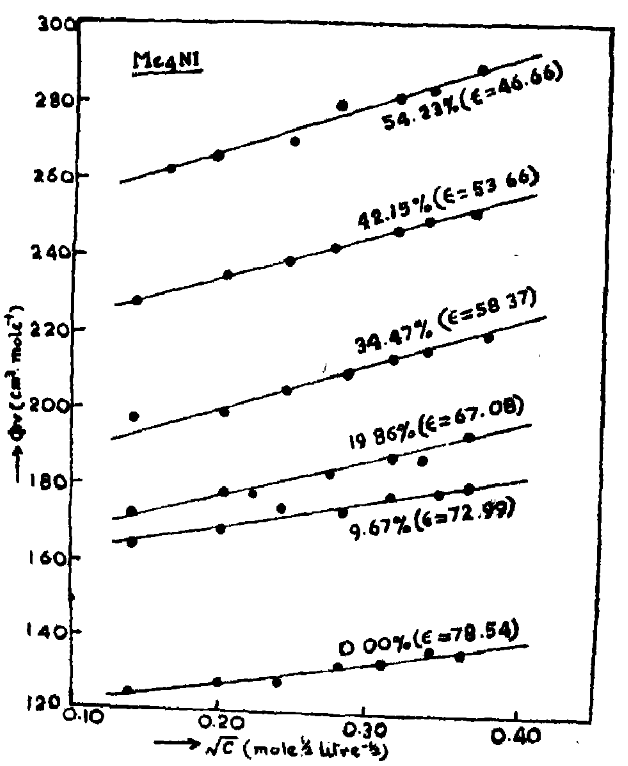


Fig. 1—Apparent molal volume, ϕ_v vs $\sqrt{C}$ curves for ME_4NI in different ethanol-water mixtures at 40°.

* To whom correspondence should be made.

usual manner[4]. Solutions of these salts in various mixtures were prepared and their densities at 40° were determined in the manner described previously[8]. Due to solubility restrictions, investigation had to be confined to smaller members viz., Me_4NI, Et_4NI, Pr_4NI and Bu_4NI, of the P_4NI series of salts the larger ones being almost insoluble.

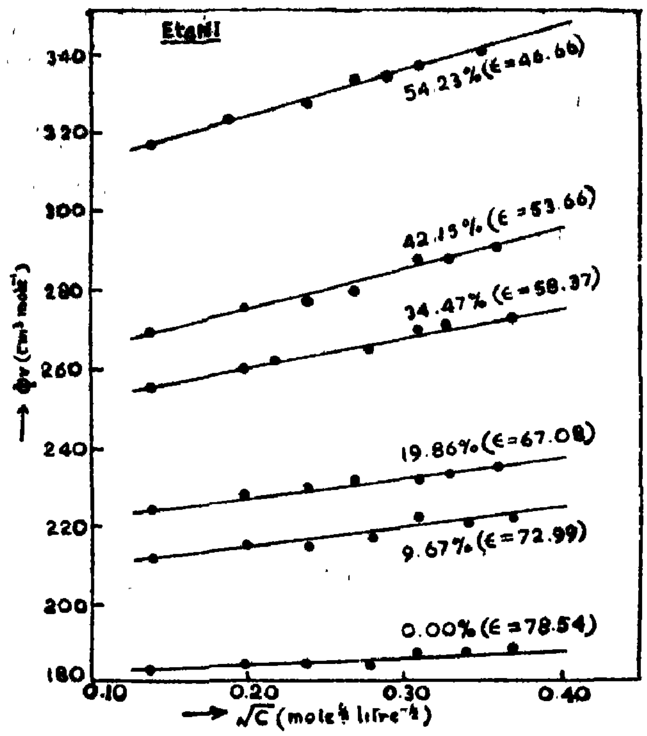


Fig. 2—Apparent molal volume, ϕv vs $\sqrt{C}$ curves for Et_4NI in different ethanol-water mixtures at 40°.

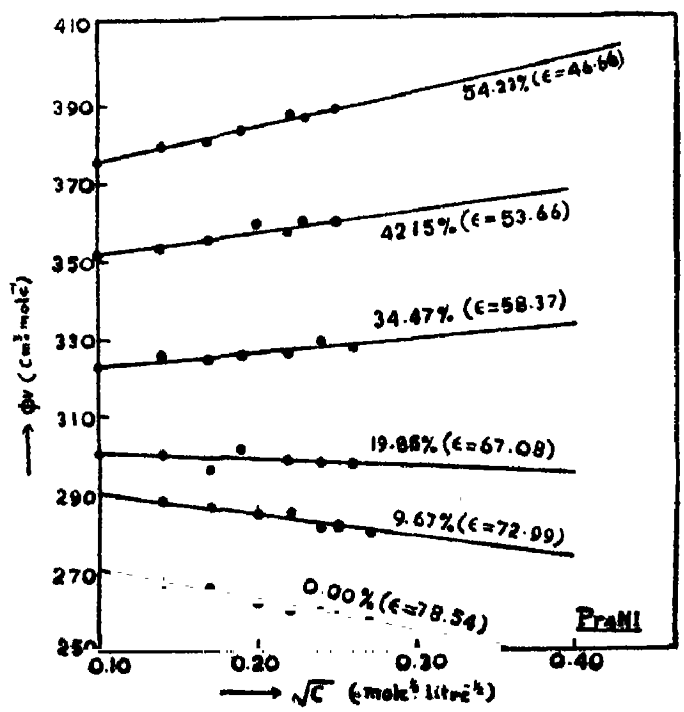


Fig. 3—Apparent molal volume, ϕv vs $\sqrt{C}$ curves for Pr_4NI in different ethanol-water mixtures at 40°.

Results and Discussion

From the density data, thus obtained, the apparent molar volumes ϕ_v of different salts in various mixtures were calculated and the ϕ_v vs $\sqrt{C}$ curves were drawn (Figs 1-4).

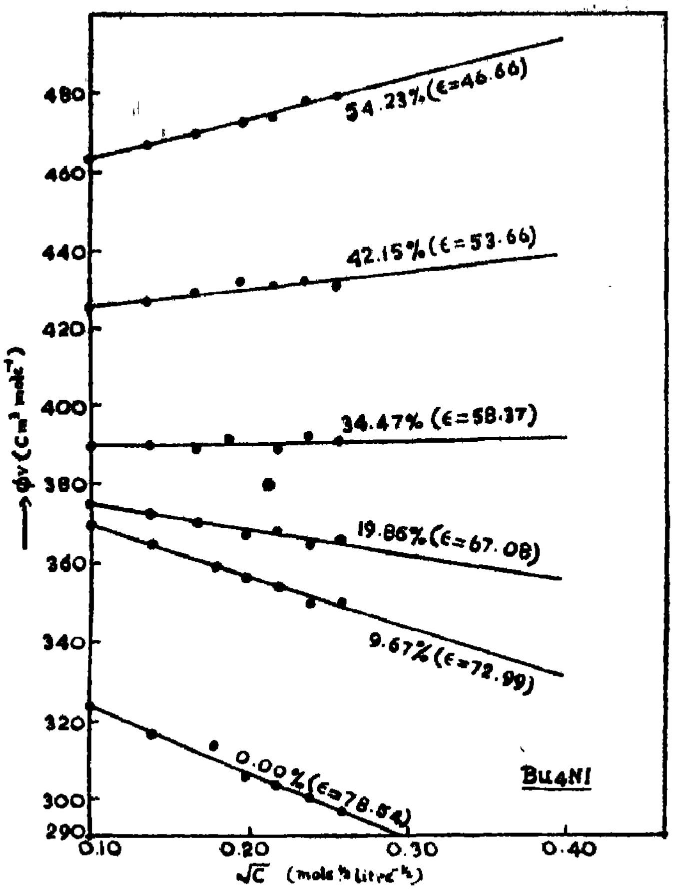


Fig. 4—Apparent molal volume, ϕv vs $\sqrt{C}$ curves for Bu_4NI in different ethanol-water mixtures at 40°.

It may be noted from the figures that for the Me_4NI and Et_4NI salts, the slope is positive although it appears to decrease with the increase in the dielectric constant of the medium ; for Pr_4NI and Bu_4NI salts, the positive slope at the lower dielectric constant becomes actually negative at higher dielectric constants. This fact is brought out more explicitly by plotting the slope S_v against the dielectric constant (Fig. 5).

It is interesting to note from Figure 5 that the slope S_v decreases smoothly with the increase in the dielectric constant. The change-over of the slope from positive to a negative value for the Pr_4NI and Bu_4NI salts, occurs around dielectric constants as 63-64 and 58-59 respectively. The slopes for Me_4NI and Et_4NI remain positive even at 80 (pure water) although extrapolation of the respective curves give 100 and 89 as the dielectric constants at the transition point in the two cases. Compared at these values, the same point for these respective salts occurs in dioxane-water mixtures around 100

(estimated), 74 (estimated), 68 and 57 and in ethanol-water mixtures around 90 (estimated), 86 (estimated), 63 and 58. It is interesting to note that these transition point dielectric constants, as observed for Pr_4NI and Bu_4NI, in all the three solvent mixtures, are very nearly the same although the estimated values for the similar transition points for Me_4NI and Et_4NI differ somewhat in the three systems and appear to be erratic.

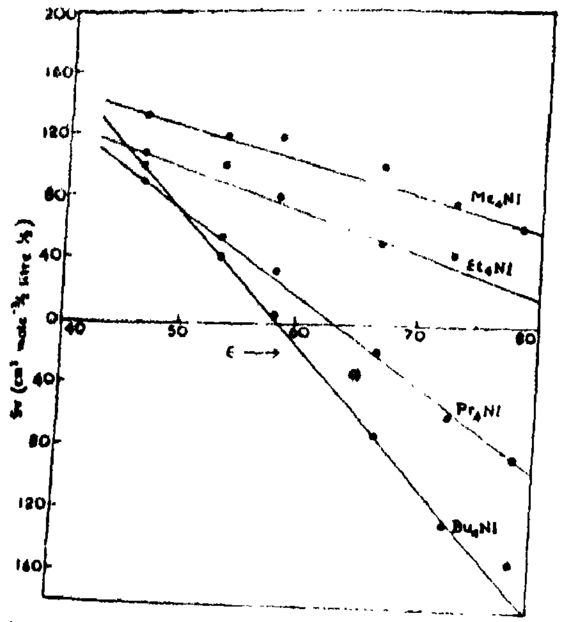


Fig. 5—Dependence of the slope S_v on the Dielectric Constant, ε in Ethanol-water mixtures at 40°.

The results seem to suggest that the constituents of solvent medium appear to play only a secondary role in determining the nature of the slope S_v (positive or negative); it is only the dielectric constant of the medium which matters.

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The Evaluation of the Thermodynamic Parameters of Viscous Flow. Aqueous Solutions of Some Organic Electrolytes

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The thermodynamic parameters of viscous flow, namely : ΔE^*, ΔF^* and ΔS^* at 25° have been calculated for aqueous solutions of four tetraalkyl ammonium bromides and four amino acids, from temperature coefficient data of respectively (i) Kay and coworkers, and England and Pilling, and (ii) Devine and Lowe, together with the apparent molal volume values at 25° reported by Wen and Saito. Nightingale and Benck's equations based on the application of Eyring's theory of absolute reaction rates, have been used. Also, only ΔE^* values at 25° have been calculated from the temperature coefficient data of Tamaki for aqueous solutions of alkyl sulphates, and $\Delta E^* - \Delta E^*_0$ calculated similarly from the data of Rastogi for N-methyl formamide solutions of tetra alkyl ammonium iodides.

EYRING and coworkers[1] have applied the theory of absolute reaction rate to the phenomenon of viscous flow. The energy of activation for viscous flow ΔE^* is found to be given by

$$\Delta E^* = R\frac{d \ln \eta}{d(1/T)} \qquad \ldots \quad (1)$$

The free energy of activation for viscous flow ΔF^* is given by

$$\Delta F^* = RT \ln\frac{\eta V}{hN} \qquad \ldots \quad (2)$$

V being the volume of one mole of solution particles, the other symbols having their usual meaning. Nightingale and Benck[2] have made use of Eyring's idea to interpret the influence of strong electrolytes upon the viscous property of solvents, as summarised in the Jones-Dole equation :

$$\eta/\eta_0 = 1 + A\sqrt{C} + BC \qquad \ldots \quad (3)$$

Neglecting the small $\sqrt{C}$ term which has its origin in interionic attraction[3], the Nightingale-Benck equation for activation energy of viscous flow is :

$$\Delta E^* = R\frac{d \ln \eta_0}{d(1/T)} + R\frac{d \ln (1+BC)}{d(1/T)} \qquad \ldots \quad (4)$$

while the viscous flow free energy is given by the equation already given (equation 2). Assuming further the activation enthalpy to be approximately equal to the activation energy, the expression for entropy of activation is obtained as

$$\Delta S^* = \frac{\Delta E^* - \Delta F^*}{T} \qquad \ldots \quad (5)$$

Thus, the temperature coefficient of viscosity B-coefficient of ionic solutions can be made use of to calculate the parameters ΔE^*, ΔF^*, ΔS^* associated with the viscous flow properties of ionic solutions.

Nightingale *et al*[2,4] made use of the temperature coefficient data for the viscous flow of solutions of (i) a number of 1-1 and 2-1 electrolytes (Kaminsky[5], Gurney[6]), and (ii) tetraalkyl ammonium bromides [Nightingale[4] : tetramethyl ; Laurence and Wolfenden[7] : tetra-ethyl ; International Critical Tables[8] : tetrapropyl ; Goldberg and Fuoss[9] : tetrabutyl] to calculate the values of the associated parameters mentioned. The approach of Nightingale and Benck has been utilised by Japanese workers[10] who have investigated the temperature coefficient of viscous flow of sodium alkyl sulphates and alkyl trimethyl ammonium bromides, and calculated the corresponding parameters.

Kay and coworkers[11] have subsequently reported viscosity measurements for tetraalkyl bromides and iodides in H_2O, D_2O, CH_3OH, CH_3CN solutions at various temperatures between 0°-65°. Their data for tetraalkyl ammonium bromide and iodide salts in aqueous solutions have been used by Mandal, Seal and Basu[12] to calculate the corresponding energy of activation only. Devine and Lowe[13] have reported viscosity measurements for amino acid solutions at different temperatures.

England and Pilling[14] have reinvestigated the temperature coefficient of viscosity B-coefficient of rather concentrated aqueous solutions of tetraalkyl ammonium bromides.

In view of the current interest in the solvent structure promoting or destroying properties of various solutes as inferred from the study of tem-

perature coefficient of viscous flow, it is imperative to procure and scrutiny critically all information regarding the various parameters associated with such processes. It is the purpose of the present note to present the results of calculation of the parameters ΔE^*, ΔF^*, ΔS^* for four tetraalkyl ammonium bromides and four amino acids, as calculated from temperature coefficient data of viscosity B-coefficient reported respectively by : (i) Kay and coworkers (K)[11], and Eagland and Pilling(EP)[14] and (ii) Devine and Lowe[13].

Calculations and Results

The values of the B-coefficient of four tetraalkyl ammonium bromides have been reported by Kay and coworkers at 10°, 25°, 45° and 65°. Eagland and Pilling[14] have apparently interpolated these data to obtain the values at 15°, 20°, 25°, 30° and 35° ; in addition they have reported their own actual measurements at these five temperatures. For comparison, the two sets of B values are shown in Table 1. [Unfortunately, our own interpolation from Kay's results would lead to values somewhat different (generally lower) from those similarly obtained by E. P[14]. Moreover, our computerised least square $(\eta/\eta_0 - 1)/\sqrt{C}$ *vs.* $\sqrt{C}$ plots for those temperatures where such plots are possible from Kay's reported viscosity data 45° and 65° for $(CH_3)_4NBr$; 10°, 45°, 65° for $(C_2H_5)_4NBr$; 10°, 25°, 45°, 65° for $(C_3H_7)_4NBr$; and 0°, 10°, 25°, 45°, 65° for $(C_4H_9)_4NBr$) lead to yet different B values].

The data for tetramethyl ammonium bromide at 20°, 25°, 30° reported by Nightingale are also shown alongwith.

The (1+B) vs. 1/T plots were made on a suitable scale. Besides the plots (over 15°-35° range) from the two sets of tabulated B – T data [(i) EP's, and (ii) Kay's, interpolated by EP], plots have also been made (over 10°-65°) using B values (1) reported by Kay himself ; as also (2) computer calculated by us from Kay's viscosity data as mentioned above.

For any particular system out of the four, there is varying degree of agreement between the different plots. For the propyl and butyl salts a nearly parallel run is found (butyl : largest positive slope) ; for the ethyl salt the mutual agreement between EP's and Kay's data is poorest, although Kay's when computerised approach EP's closely. For the methyl salt all plots are moderately close together (EP's interpolation from Kay's data leads to greater scatter), showing an almost parallel run with negative slope. Nightingale's data for this system also show a linear fall, though of much larger negative slope. Nightingale's results, which show

TABLE 1

B-COEFFICIENT DATA OF DIFFERENT WORKERS AT VARIOUS TEMPERATURES FOR TETRA ALKYL AMMONIUM BROMIDES

Temp. °C	$(CH_3)_4NBr$					$(C_2H_5)_4NBr$				$(C_3H_7)_4NBr$				$(C_4H_9)_4NBr$			
	a	b	c	d	e	a	b	c	d	a	b	c	d	a	b	c	d
0°																1.68	1.67
10°			0.058					0.38	0.414			0.98	1.06			1.46	1.44
15°	0.085	0.075	0.067*			0.398	0.39	0.365*		0.915	0.93	0.92*		1.41	1.41	1.38*	
20°	0.098	0.090	0.076*		0.0627	0.386	0.36	0.352*		0.870	0,870	0.86*		1.36	1.32	1.305*	
25°	0.098	0.083	0.083		0.1014	0.381	0.34	0.34		0.820	0.820	0.820	0.84	1.26	1.24	1.24	1.20
30°	0.105	0.095	0.088*		0.187	0.368	0.33	0.328*		0.773	0.77	0.758*		1.20	1.18	1.17*	
35°	0.108	0.100	0.092*			0.355	0.32	0.32*		0.738	0.73	0.71*		1.14	1.12	1.10*	
45°			0.10	0.104				0.30	0.341			0.64	0.69			0.99	0.86
65°			0.11	0.118				0.27	0.295			0.54	0.54			0.83	0.82

a.—EP's data[14].
b.—Kay's, interpolated by EP[14],
c.—Kay's own, together with our interpolation(*) from Kay's.
d.—Kay's, computerised by us.
e.—Nightingale's[4].

* The ΔE^* values calculated from the $(\Delta E + \Delta E^*)$ values reported by Mandal, Seal and Basu[13], who have utilised the same data for the calculation, are quite close (the largest difference is only 5% for the ethyl salt). The slight difference may be attributed to the difference in (1+B) vs. 1/T plot ; ours were made on suitably large scale and showed up the deviations from linearity.

Also, the η_0 values for water at different temperatures were taken from ref. (15)

very little scatter, appear to be by far the most accurate, in as much as care has been taken to ensure that the intercept A of equation(3) in the $\left(\frac{\eta}{\eta_0}-1\right)/\sqrt{C}$ vs. $\sqrt{C}$ plot agrees with the theoretical estimate of the same. Further, Nightingale's selection of the viscosity data for the other three quarternary salts, and their proper processing (concentration scale correction) is also equally critical.

From the slopes, at 25°, of the tangents to these various (1+B) vs. 1/T plots, the quantities $\triangle E^*$ at 25° were calculated according to equation (4), using the value of $\triangle E^*_0$ calculated similarly from the slope at 25° of the log η_0 vs. 1/T plot for water*.

$$\triangle E^*_0 = R\frac{d \ln \eta_0}{d(1/T)} \qquad \ldots (6)$$

The $\triangle E^*$ values thus calculated from the two sets of data (namely : (1) EP's. and (2) K's, computerised by us) are reported in Table 2, together with the values calculated by Nightingale.**

For the calculation of the free energy of activation of viscous flow at 25° according to equation (2) the viscosity coefficient η and the volume V must be known. The η values are easily calculated by the Jones-Dole equation (3) (neglecting the $\sqrt{C}$ term), using the reported B-value for the solutions at 25°. The volume (in cc) of one mole of solution particles(V) is given by

$$V = \frac{1000}{n_1 + \nu n_2} \qquad \ldots (7)$$

where ν is the number of species into which a solute molecule dissociates, and n_2 is the number of moles of solute per liter of solution (molarity of solution). The number of moles of solvent per liter of solution n_1 is given by

$$n_1 = \frac{1000\rho - n_2 M_2}{M_1} \qquad \ldots (8)$$

where M_1 and M_2 are the molecular weights of the solvent and solute respectively. The densities ρ of the different solutions at 25° (reported only by Eagland *et al* in the microfilm edition of the *J. Phys. Chem.*) have been calculated by using the values of the apparent molal volumes at 25° of the same solutes, as reported by Wen and Saito[16], by means of the expression

$$\phi = \frac{1}{m}\left(\frac{1000 + mM_2}{\rho} - \frac{1000}{\rho_0}\right) \qquad \ldots (9)$$

TABLE 2

VALUES OF VISCOUS FLOW PARAMETERS FOR TETRAALKYL AMMONIUM BROMIDE AND AMINO ACIDS AT 25°

Solutes	$\triangle F^*$(K cals) a	b		$\triangle E^*$(K cals.) a	b		$\triangle S^*$ (e.u.) a	b	
$(CH_3)_4NBr$	2.295	2.290	2.30[c]	3.813	3.802	2.85[c] (2.815)	5.1	5.075	1.85[c]
$(C_2H_5)_4NBr$	2.463	2.465	2.44[d]	4.265	4.284	4.11[d]	6.03	6.029	5.61[d]
$(C_3H_7)_4NBr$	2.677	2.684	2.75[e]	4.883	4.976	5.00[e]	7.4	7.69	7.54[e]
$(C_4H_9)_4NBr$	2.853	2.836	2.88[f]	5.072	5.105	6.05[f]	7.44	7.614	10.6[f]
Glycine		2.284			3.806			5.11	
Alanine		2.332			3.9272			5.85	
Aminobutyric acid		2.385			4.1106			5.8	
Aminohexanoic acid		2.475			4.4494			6.66	

a.—Eagland and Pilling's data[14]

b.—Kay and coworkers data[11]

c.—Nightingale's data[4]

d, e.—Laurence & Wolfenden's data[7] and International Critical Table's data[8] (though only the B values at 25° are reported in ref. 7)

f.—Thermodynamic parameters reported by Nightingale[4] after calculation from Goldberg and Fuoss's data[9] using dB/dT values from W.Y.Wen, Ph.D. thesis, Univ. of Pittsburgh, 1957.

* $\triangle F^*$, $\triangle E^*$ and $\triangle S^*$ for KCl solution calculated from Gurney's B-coefficient data at different temperatures, and density data at 25° from International Critical Tables compilation, agreed exactly with the calculated values of Nightingale, showing the accuracy of our procedure.

** Our calculated $\triangle E^*$ value for the methyl salt (from Nightingale's reported temperature coefficient data for B-coefficient of this salt only) is shown alongside Nightingale's own calculated values for this salt, to show the extent of agreement between the two calculations.

'm' being the molality of the solution, and ρ_0 the density of the pure solvent (0.99707 gm/cc). The reported ϕ values of one molal solution at 25° were used.

The calculated η and V values for one molal solution at 25° were used in equation (2) to calculate the corresponding ΔF^* values*. The ΔF^* values thus obtained from the data of the two groups of workers together with Nightingale's calculated values are reported in Table 2.

Finally, assuming the energy and enthalpy of activation to be identical, the ΔS^* values were calculated from the ΔE^* values obtained above, using equation (5). These, obtained from the data of the two groups of workers, together with the values calculated by Nightingale, are also shown in Table 2.

Calculation for amino acid solutions

The viscosity B-coefficient for four different amino acid solutions as obtained from measurements over the concentration range 0.1 to 0.5*M*, at 15° and 25°, have been reported by Devine and Lowe[16]. From the slopes of the corresponding (1+B) vs, 1/T plots, the ΔE^* values were determined as before. The slope increases steadily from glycine (negative slope) through alanine (slightly negative) and amino butyric acid (positive) to amino hexanoic acid (largest positive). The earlier value for the slope d ln η_0/d(1/T) was used. The density values for one molal solutions at 25° were obtained directly by means of the equation given by these authors, using the reported α and β coefficient values,

$$d = d_0 + \alpha m + \beta m^2$$

Our earlier used ρ_0 value at 25°, which has been used here also, is identical with the value used by the authors.

The calculated ΔF^*, ΔE^*, ΔS^* values have been reported in Table 2.

Calculation of ΔE^* for alkyl sulphates in aqueous solutions and $(\Delta E^* - \Delta E_0^*)$ for tetraalkyl ammonium iodides in NMF solutions.

In addition to the data used above, for which complete calculation of all three quantities ΔF^*, ΔE^*, ΔS^* could be carried through, there are data recorded in the literature only for the temperature variation of B-coefficient of some systems, wherefrom ΔE^* can be calculated; however, the density value at none of the working temperatures is recorded, so that ΔF^* and ΔS^* cannot be calculated. Such are the data recorded by Tamaki *et al*[17] for the temperature variation of B-coefficient of some alkyl sulphates in aqueous solution, generally at three different temperatures over the range 10°-50°. The ΔE^* calculation at 25° from the slope of the (1+B) vs. 1/T plot using ΔE_0^* value is straightforward; the results are recorded in Table 3. Rastogi's data[18] for the temperature variation of B-coefficients of tetraalkyl ammonium iodide in N-methyl formamide at 25°, 30° and 35° are interesting in so far as these pertain to non-aqueous solvent; the density values at any temperature being unrecorded, ΔF^* and ΔS^* calculation and their comparison with the corresponding quantities in aqueous solution cannot be carried through. The ΔE^* calculation is again straightforward, and the results are shown in Table 3.

TABLE—3 $\Delta E^* - \Delta E_0^*$ FOR TETRAALKYL AMMONIUM IODIDES IN N-METHYL FORMAMIDE AND ΔE^* FOR SODIUM ALKYL SULPHATES IN WATER AT 25°

Alkyl ammonium iodides	$\Delta E^* - \Delta E_0^*$(25°) (K cals)	Sodiumalkyl sulphate (in water)	ΔE^* (25°) (K cals)
Me_4NI	−1.388	Methyl sulphate	3.9188
Et_4NI	−0.9478	Ethyl sulphate	3.9679
Pr_4NI	−0.7539	Propyl sulphate	4.1679
Bu_4NI	−0.6987	Pentyl sulphate	5.2400
Pen_4NI	−0.5475		
Hex_4NI	−0.4882		
Hep_4NI	−0.3870		

Discussion

From the results presented in columns (c) and (d) of Table 1 it is seen that the very first step in the processing of viscosity data, namely plot of $(\frac{\eta}{\eta_0} - 1)/\sqrt{C}$ *vs.* $\sqrt{C}$ leads to somewhat different B values according as we consider the result of (i) Kay's own plot of his data (column c), and (ii) our computerised least square plot of the same data (in the few cases, enumerated earlier, where this is possible; column d, Table 1). The B values obtained by us are somewhat higher (5-10% generally) than

those reported by Kay, for the methyl, ethyl and propyl salts, while for the butyl salt they are almost same (or, our's even somewhat smaller). However, we do not consider further these results of our processing, because, they are too few in number.

The result of interpolation from the plot of (Kay's) B vs. T, so as to yield the B values at intermediate temperatures not considered by Kay (15°, 20°, 30°, 35°) as reported by Eagland and Pilling (column b), are, surprisingly, different from the result of our interpolation from the same data (column c, data marked*). E.P.'s values are generally higher (most marked for the methyl salt, ~ 10%). (We prefer to consider our interpolation results more reliable, and do not further consider E.P.'s interpolation results). Also, Eagland-Pilling's own data for all the salts at all the five temperatures investigated by them (15, 20, 25, 30, 35°), are higher than Kay's results [Kay's own, at 25°; together with our interpolated results (15, 20, 30, 35°) from Kay's wider temperature range (10, 25, 45, 60°) study]. E.P.'s results are ~ 15-20% higher for the methyl salt, and ~ 10-15% higher for the ethyl salt, while less so for the propyl and butyl salts.

The comparison thus boils down to that between the performance in the further calculations, of the data of Eagland-Pilling, and Kay, as presented respectively in columns (a) and (c) of Table 1. To this must be added the performance of Nightingale's accurate data for the methyl salt (column e). (These B values are significantly different from either the (a) or the (c) column values : ~20% less at 20°, and 35% higher at 30°; so that the slope of the corresponding (1+B) vs. 1/T plot giving the $\triangle E^*$ value, is also significantly higher). The thermodynamic parameters calculated from these, shown respectively in columns (a) and (b) of Table 2 for each of the four tetraalkyl salts, and the set marked (c) for the tetramethyl salt only, lead to the following conclusions :

(1) The values of the primary calculated quantities $\triangle E^*$ and $\triangle F^*$ (and therefore also that of the derived quantity $\triangle S^*$) are not significantly different, as obtained from (i) Eagland-Pilling and (ii) Kay's data (maximum difference: ~4%: generally much less). The evaluation of these quantities is thus found to be not significantly sensitive to the processing procedure of the primary viscosity data $\left(\frac{\eta}{\eta_0}-1\right)/\sqrt{C}$ *vs.* $\sqrt{C}$ plot, (1+B) *vs.* $\frac{1}{T}$ plot, etc.), provided of course that the processing is reasonably good.

(2) On the other hand, Nightingale's data for the methyl salt leads to significantly smaller (~30%) $\triangle E^*$ value for this salt. The $\triangle F^*$ value is, however, not significantly altered ; so that as a result, the calculated $\triangle S^*$ is also markedly (~ 6%) lower.

(3) The thermodynamic parameters calculated for the ethyl and propyl salts from Lawrence-Wolfenden's, and the International Critical Tables' results respectively for these salts (sets marked 'd' and 'e' respectively in Table 2) are, however, not markedly different from those calculated from Kay's or E.P.'s data. Only the $\triangle S^*$ value for the ethyl salt shows any difference at all (~6% lower).

(4) Finally, for the butyl salt, the $\triangle E^*$ value reported by Nightingale from Goldberg-Fuoss's data, is significantly higher (~20%) than that calculated from E.P.'s or Kay's data. The $\triangle F^*$ value is, as before, almost same ; so that the calculated $\triangle S^*$ value is markedly higher (~30%).

The further discussion of the relative contribution of these calculated enthalpic and entropic changes to the solvent structure-making or structure-breaking characteristics of these quarternary ammonium ions is clearly outside the scope of the present study, which is only restricted rather to the precise determination of the values of these thermodynamic parameters from viscosity measurements, and the critical appraisal of these values when available from different studies. The only significant point to be emphasised in connection with such discussions, as emerges from the present study, is the need for such a critical appraisal ; because, as shown above, the magnitudes of both the enthalpic and entropic changes for the same salt as calculated from the results of different investigators, may be markedly different (e.g., for the methyl and butyl salts, above). Consequently, reliable and useful pronouncements regarding the relative importance of these two factors in the process of modification of the solvent structure by the concerned quarternary ammonium cation (or for that matter, any other cation) as revealed by viscosity studies, can only then be made when the values of the associated thermodynamic parameters which form the basis of such discussions, have first been critically appraised.

Unlike the quarternary ammonium salts considered, the values of the thermodynamic parameters for the viscous flow process of the four different amino acids are available from one study only. A slow increase of the entropic change factor with the bulk size of the zwitterion considered, is noteworthy.

Finally, for the tetraalkyl ammonium iodides and the sodium alkyl sulphates, considered in Table 3, the results are obviously incomplete, in so far as in absence of a knowledge of the concomitant $\triangle F^*$ and $\triangle S^*$ values for these organic electrolytes no meaningful discussion regarding the solvent structure promoting or destroying characteristics of these electrolytes can be undertaken. Moreover, for the quarternary ammonium iodides, besides the values of the parameters in the non-aqueous solvent investigated, parallel studies in aqueous solution would lead to the possibility of

illuminating comparative discussions of the dependence of the solvent structure modifying behaviour of any particular quarternary alkyl ammonium ion considered, on the solvent characteristics itself. Very few such comparative studies are recorded in literature.

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Ion-Solvent Interaction : Viscosity of Bromates, Iodates and Sulphates of Potassium and Sodium in Dioxane-Water Mixtures at Different Temperatures

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The viscosities of the bromates, iodates and sulphates of potassium and sodium at 10, 20 and 30% dioxane-water mixtures (by wt.) have been measured at 30, 35, 40 and 45°. The data have been analysed in terms of Jones-Dole equation : $\eta_r = 1 + AC^{\frac{1}{2}} + BC$. The values of the constants A and B indicate ion-ion and ion-solvent interaction respectively and ion-ion interaction is of the order $SO_4^{2-} > IO_3^- > BrO_3^-$ and ion-solvent interaction order is $BrO_3^- > IO_3^- > SO_4^{2-}$.

THE viscosity measurements of $KBrO_3$, $NaBrO_3$, KIO_3, $NaIO_3$, K_2SO_4 and Na_2SO_4 in dioxane-water mixtures (by wt.) have been carried out at 30, 35, 40 and 45°±0.01. The data have been interpreted in terms of Jones-Dole equation[1] :

$$\eta_r = 1 + AC^{\frac{1}{2}} + BC \quad \ldots \quad (1)$$

where η_r is the relative viscosity of the solution, C is the concentration of the electrolyte and A and B are constants. The coefficient A is due to the contribution from interionic electrostatic forces[2-4] and B gives the measure of the order or disorder introduced by the ions into the solvent structure.

A review of the literature shows that no general theory has yet been developed for B-coefficient, however, it is a manifestation of ion-solvent interaction[5]. In the present investigation, interest, therefore, centres on the coefficient of B. The nature of the B-coefficient as pointed out by Cox and Wolfenden[6] is attributed to its specific additive character depending on the constituent ions. On the other hand, Asmus[7] used the entropy of hydration to *correlate* ionic B values and recently a single relationship between the ionic B values and molar entropy of hydration has been obtained by Nightingale[8].

Experimental

All the salts used were of E. Merck 'extra pure' varieties. The SO_4^{2-} content was estimated in the usual manner[9]. The preparation of solvents and solutions were the same as described earlier[10]. The viscometric technique were the same as that of Chackravarty and Prasad[11]. The densities of the solutions and the solvents were determined by pycnometer with buoyancy correction and is same as that of Srinivasan and Prasad[12]. All sorts of precautions were taken to check the evaporation of the solvent[13]. The time of flow did not exceed 0.2 sec. in 20 minutes and have an error of ±0.04 to 0.08%. Density readings were precise up to 0.0002 g.ml^{-1}, i.e., an error up to 4 in 10^{5}. The concentration range was from 0.1 to 0.001*M*.

Results and Discussion

Viscosities of the mixed solvents as well as those containing salts solutions under study were measured. The results have been analysed in terms of Jones-Dole equation[1] as the plot of $\eta_r - 1/C^{\frac{1}{2}}$ vs. $C^{\frac{1}{2}}$ is linear. The intercept and the slope of the plot give respectively the coefficients of A and B. The coefficient A and B, thus obtained for various salts are given in Tables 1 and 2 respectively. The calculated values of A[14] are in good agreement with that of the observed one. The relative viscosities calculated from these values of A and B, are found to be in acceptable agreement with the experimental values.

A Values : The different A values (Table 1). of all six salts studied indicate dependence of ionic interactions on the nature of the electrolyte and are all positive. The electrostatic ion-ion interaction and hence the value of A is found to increase with the decrease in dielectric constant in the medium when the concentration of the dioxane increases in the mixture. From Table 1, it is seen that the ion-ion interaction is of the order $SO_4^{2-} > IO_3^- > BrO_3^-$. Further the value of A decreases with the increase in temperature for all the salts which one should expect in view of more thermal agitation at higher temperatures and reduction of attractive forces.

Dependence of B on temperature : According to Stokes and Mills[15], the viscosity of a dilute electrolytic solution incorporates that of the solvent plus the contribution from other sources. They are, η^*,

TABLE 1

$A \times 10^{3}$ / $l^{\frac{1}{2}}.mol^{-\frac{1}{2}}$

Temperature in °C	10%D	20%D	30%D	10%D	20%D	30%D
		$KBrO_3$			$NaBrO_3$	
30	6.9	7.1	8.2	7.2	7.4	8.9
35	6.2	6.6	7.9	6.3	7.0	8.2
40	5.8	6.0	7.4	5.9	6.2	7.4
45	5.4	5.8	6.9	5.5	5.9	6.3
		KIO_3			$NaIO_3$	
30	7.2	8.1	9.6	7.8	8.7	10.2
35	6.7	7.3	8.9	7.5	8.4	9.7
40	6.0	6.8	8.0	7.1	7.9	9.1
45	5.4	6.0	7.2	6.6	7.2	8.4
		K_2SO_4			Na_2SO_4	
30	13.5	16.0	26.6	13.9	16.6	17.2
35	13.0	15.0	26.0	13.4	15.2	16.0
40	12.2	14.2	24.2	12.6	14.1	14.6
45	11.6	12.6	22.2	1.21	13.4	13.9

the positive increase due to the shape and size of an ion; η^{A}, the increase due to the alignment or orientation of the polar molecules by the ionic field and η^{D}, the decrease in the viscosity arising due to the distortion of the solvent structure by the ions. Therefore, B-coefficient can be discussed in terms of these viscosity effects at different temperatures.

The B-coefficient of all the salts increases with the increase in temperature. This indicates that the viscosity decrease due to solvent structure, i.e., η^{D} is small and hence $\eta^{E}+\eta^{A}>\eta^{D}$ and B is positive. The B value is found to be of the order $SO_4^{2-}>IO_3^{-}>BrO_3^{-}$. Hence it can be concluded that the distortion of the solvent structure or ion-solvent interaction is of the reverse order, i.e., $BrO_3^{-}>IO_3^{-}>SO_4^{2-}$.

Further, also according to Stokes and Mills[15], the lesser the value of dB/dt, the greater is the ion-solvent interaction. In the present case, the plot of B vs t is linear and the slope dB/dt is found to be of the order $SO_4^{2-}>IO_3^{-}>BrO_3^{-}$. This also indicates the ion-solvent interaction to be of the order $BrO_3^{-}>IO_3^{-}>SO_4^{2-}$.

Dependence of B on the cation : Ions with greater crystal radii and small charge density, K^{+}, would have a weak orienting effect in the first layer. Therefore η^{E} and η^{A} will be small. Also there exist a considerable amount of distortion in the vicinity of such ions due to the competition between the ionic field and bulk structure and consequently η^{D} will be large. Thus B will be smaller for K^{+} salts than for Na^{+} salts (Table 2). So the order of ion-solvent interaction is $K^{+}>Na^{+}$.

Dependence of B on dioxane content : McRae[16] has suggested that the dioxane molecule has two non-adjacent dipolar group whose moment cancel, so that the effective reaction field is probably greater than is indicated by microscopic properties. Hence the frozen layer, as suggested by Frank and Evans[17], around the cation be expected to be constituted of both the water molecules and the dioxane molecules,

TABLE 2

B/l. mol^{-1}

Temperature °C		$KBrO_3$			$NaBrO_3$	
30	0.030	0.042	0.062	0.065	0.089	0.104
35	0.043	0.059	0.078	0.089	0.109	0.119
40	0.058	0.076	0.098	0.104	0.122	0.134
45	0.074	0.092	0.114	0.122	0.138	0.146
		KIO_3			$NaIO_3$	
30	0.120	0.145	0.165	0.181	0.212	0.252
35	0.152	0.164	0.175	0.210	0.235	0.264
40	0.165	0.185	0.220	0.235	0.255	0.281
45	0.185	0.204	0.245	0.268	0.278	0.295
		K_2SO_4			Na_2SO_4	
30	0.248	0.275	0.348	0.262	0.291	0.385
35	0.280	0.300	0.380	0.300	0.325	0.410
40	0.305	0.330	0.415	0.330	0.352	0.438
45	0.330	0.358	0.434	0.360	0.378	0.448

possibly consisting more of the former than the latter kind of molecules ; whereas the diffused layer would consist of loosely oriented water and dioxane molecules, the extent of orientation decreasing with the distance from the ion till the outermost layer has the same structure and composition as that of the solvent. When the dioxane content of the solvent increases, more dioxane molecules take part in constituting the diffused layer and thus promoting a sort of ordering effect in the solvation sphere and hence would lead to larger values of η^{E} and η^{A} and exhibit an increase in the value of B with increase in dioxane content (Table 2).

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Transference Number of Hydrochloric Acid in Dioxane-Water Mixtures from Electromotive Force Measurements

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Transference number of hydrochloric acid was determined from the study of the cell : Ag-AgCl | HCl (m_1) dioxane X% water Y% ⋮ HCl (m_2) dioxane X% water Y% | AgCl-Ag temperature range 25-45°, where the weight per cent of dioxane was 10, 30, 40 and 60. The data at 25° compares well with those determined by Hittorf's method in the same solvent mixture.

IN aqueous solution, most of the ions are hydrated and it is expected that water will be transported to the electrodes during electrolysis. Washburn number[1] gives an idea about the number of moles of water transported by the electrolyte from the anode to cathode on the passage of one faraday of electricity. It also provides valuable information on the preferential (or non-preferential) presence of water or the non-electrolytic solvent (in case of mixed solvents) in the solvation shells of the ions[2,3]. The determination of Washburn number using Feakin's method[3] for mixed solvent systems involving dioxane-water mixtures of various compositions requires a knowledge of cation transference number (t_+) of HCl in these solvent mixtures. So in the present investigation, the cationic transference number of hydrochloric acid in these solvent mixtures containing 10, 30, 40 and 60 weight per cent of dioxane has been determined at 25, 30, 35, 40 and 45° from the e.m.f. measurement of the cell ;

Ag-AgCl | HCl (m_1) dioxane X% water Y% ⋮ HCl (m_2) dioxane X% water Y% | AgCl-Ag

(Cell-I)

The accuracy of the results were checked up in measuring the transference number by Hittorf's method at 25° three suitable concentrations of the electrolyte corresponding to each concentration of the solvent.

Experimental

Dioxane used was BDH AnalaR quality and was purified as described elsewhere[4]. Hydrochloric acid used was a Kahlbaum sample, which was diluted, distilled, the middle fraction of a constant boiling mixture was collected and was used as a stock solution to prepare solutions of desired concentration. The chloride content of the stock solution was analysed gravimetrically. All solutions were prepared in the molal scale. Ag-AgCl electrode used was of thermal electrolytic type. An air thermostat was used in which the temperature was regulated within ±0.05°. A Leeds-Northrup K-2 type potentiometer was used in conjugation with a matching galvanometer and calibrated standard cell.

The solutions in the above cell were separated by means of a stop cock of equal bore as the connecting tubes of the half cells. The cell assembly was kept inside an air thermostat maintained at the desired temperature. The connecting stop cock was opened carefully so as to establish contact between the two half cells and the e.m.f. readings were taken. Duplicate experiments were performed simultaneously in each case and the duplicates generally agreed within ±0.1 mV. The reported e.m.f. values are the mean of the duplicates.

In determining the transference number independently by Hittorf's method, an apparatus similar to that used by Washburn[5] was used. The other experimental procedures were followed in the usual manner.

Results and Discussion

When the concentrations of the solutions in the two half cells are 'm' and (m+dm), the e.m.f. of the cell I is given by

$$dE_t = 2t_+ \frac{RT}{F} d \ln a \quad \ldots (1)$$

$$\text{or,} \quad \frac{dE_t}{d \log a} = 2 \times 2.3026 \frac{RT}{F} t_+ \quad \ldots (2)$$

where 'a' is the mean activity of the electrolyte at concentration 'm', t_+ is the transference number of HCl. The values of E_t, the e.m.f. of the cell-I when the concentration 'm_1' was fixed at 0.03*M* and 'm_2' was varied between 0.003*M* to 0.1 *M*, are reported in Table 1.

TABLE 1

E.M.F. OF THE CELL-I IN ABSOLUTE VOLTS

Solvent : 10% dioxane + 90% water

m	25°C	30°C	35°C	40°C	45°C
0.003	−0.09250	−0.09335	−0.09480	−0.09570	−0.09650
0.004	−0.08090	−0.08205	—	—	—
0.005	−0.07185	−0.07265	−0.07350	—	−0.07480
0.006	−0.06460	−0.06535	−0.06590	−0.06645	−0.06705
0.007	−0.05835	−0.05900	−0.05900	−0.05995	−0.06045
0.008	−0.05300	−0.05360	—	—	—
0.009	−0.04820	−0.04880	−0.04925	−0.04970	−0.05010
0.010	−0.04395	−0.04450	−0.04470	−0.04510	−0.04550
0.020	−0.01620	−0.01640	−0.01710	−0.01730	−0.01740
0.040	0.01150	0.01155	0.01250	0.01270	—
0.050	0.02035	0.02055	0.02105	0.02130	0.02145
0.060	0.02765	0.02790	0.02860	0.02900	0.02915
0.070	0.03375	0.03405	0.03470	0.03520	0.03545
0.080	0.03825	0.03945	0.04005	0.04060	0.04085
0.090	0.04375	0.04405	0.04500	0.04565	0.0 —
0.100	0.04710	0.04840	0.04940	0.05025	0.05085
30% dioxane + 70% water					
0.003	−0.09030	−0.09125	−0.09195	−0.09270	−0.09350
0.004	—	−0.07970	−0.08025	−0.08090	−0.08155
0.005	−0.07000	−0.07230	−0.07120	−0.07180	−0.07200
0.006	−0.06280	−0.06340	−0.06380	−0.06430	—
0.007	−0.05670	−0.05725	−0.05755	−0.05805	−0.05850
0.008	−0.05140	−0.05195	−0.05225	−0.05265	−0.05305
0.009	−0.04685	−0.04730	—	−0.04790	—
0.010	−0.04270	−0.04310	−0.04330	−0.04370	−0.04405
0.020	−0.01570	−0.01585	−0.01600	−0.01610	−0.01625
0.040	0.01110	0.01115	—	0.01175	0.01190
0.050	0.01970	0.01985	0.02000	0.02010	0.02030
0.060	0.02660	0.01690	0.02705	0.02730	0.02745
0.070	0.03430	0.03290	0 03305	0.03335	0.03350
0.080	0.03775	0.03800	0.03830	0.03860	0.03890
0.090	0.04230	0.04260	0.04280	0.04320	0.04345
0.100	0.04640	—	0.04690	0.04730	—
40% dioxane + 60% water					
0.003	−0.08705	−0.08800	−0.08870	−0.08940	−0.08985
0.004	−0.07595	−0.07670	−0.07800	−0.07790	−0.07835
0.005	−0.06735	−0.06800	−0.06795	−0.07000	−0.06970
0.006	−0.06035	−0.06100	−0.06105	—	−0.06230
0.007	−0.05450	−0.05510	−0.05520	−0.05590	−0.05615
0.008	−0.04950	−0.04995	−0.05010	−0.05060	−0.05090
0.009	−0.04495	−0.04545	−0.04560	—	−0.04630
0.010	−0.04095	−0.04150	−0.04155	−0.04195	−0.04220
0.020	−0.01500	−0.01525	−0.01530	−0.01540	−0.01545
0.040	0.01065	0.01070	0.01095	0.01085	0.01095
0.050	0.01885	0.01955	0.01910	0.01930	0.01940
0.060	0.02560	0.02580	0.02630	0.02615	0.02625
0.070	0.03120	0.03145	0.03180	0.03200	0.03210
0.080	—	0.03640	0.03685	0.03695	0.03710
0.090	—	0.04080	0.04025	0.04135	0.04155
60% dioxane + 40% water					
0.003	−0.07625	−0.07670	—	—	—
0.004	−0.06625	−0.06680	−0.06640	−0.06720	−0.06680
0.005	−0.05870	−0.05915	−0.05875	−0.05950	−0.05920
0.006	−0.05165	−0.05300	−0.05250	−0.05320	−0.05295
0.007	−0.04730	−0.04770	−0.04740	−0.04795	−0.04775
0.008	−0.04290	−0.04330	−0.04295	−0.04350	−0.04330
0.009	−0.03900	−0.03935	−0.03905	−0.03960	—
0.010	—	−0.03580	−0.03560	−0.03610	−0.03585
0.020	−0.01315	−0.01330	−0.01335	−0.01350	−0.01345
0.040	0.00910	0.00945	0.00940	−0.00935	—
0.050	0.01670	0.01690	0.01680	0.01685	0.01670
0.060	0.02250	0.02275	0.02280	0.02290	0.02265
0.070	0.02770	0.02790	0.02775	0.02800	0.02800
0.080	0.03200	0.03235	0.03220	0.03280	0.03240
0.090	0.03570	0.03680	0.03635	0.03680	0.03755
0.100	0.03980	0.03995	—	0.04035	0.04095

MacInnes and Beattie[8] have suggested that the values of E_t could be expressed as a function of the logarithm of the activities of the electrolyte. To calculate the activity at different concentrations a knowledge of activity coefficient at these concentrations are necessary. The activity coefficient values for the different concentrations used here are reported elsewhere from this laboratory[7].

The present set of data for E_t were found to fit in an equation of the type :

$$E_t = K_1 + K_2 \log a + K_3 (\log a)^3 \qquad \ldots (3)$$

where K_1, K_2 and K_3 are empirical constants and 'a' is the mean activity of HCl at molality m_2. The equation (3) on differentiation with respect to log a, becomes

$$\frac{dE_t}{d \log a} = K_2 + 3K_3 (\log a)^2 \qquad \ldots (4)$$

So from equations (2) and (4)

$$t_+ = \frac{K_2}{2k} + \frac{3}{2}\frac{K_3}{k} (\log a)^2 \qquad \ldots (5)$$

where 'k' equals 2.3026RT/F.

The transference number so determined are recorded in Table 2. The constants of the equation (3) were calculated by the least square method and are recorded at the bottom of the Table 2.

TABLE—2

TRANSFERENCE NUMBER OF HCl IN DIOXANE-WATER MIXTURE

1 % dioxane + 90% water

m	25°C	30°C	35°C	40°C	45°C
0	0.8195	0.8150	0.8125	0.8045	0.7995
0.003	0.8251	0.8205	0.8180	0.8115	0.8071
0.004	0.8262	0.8216	—	—	—
0.005	0.8270	0.8224	0.8200	—	0.8099
0.006	0.8276	0.8231	0.8207	0.8155	0.8108
0.007	0.8281	0.8236	0.8212	0.8164	0.8115
0.008	0.8285	0.8240	—	—	—
0.009	0.8289	0.8244	0.8221	0.8176	0.8120
0.010	0.8292	0.8248	0.8224	0.8181	0.8132
0.020	0.8311	0.8267	0.8245	0.8212	0.8159
0.040	0.8328	0.8283	0.8263	0.8240	—
0.050	0.8333	0.8288	0.8267	0.8247	0.8191
0.060	0.8336	0.8292	0.8272	0.8253	0.8196
0.070	0.8339	0.8295	0.8274	0.8257	0.8200
0.080	0.8341	0.8297	0.8276	0.8261	0.8203
0.090	0.8344	0.8299	0.8279	0.8264	—
0.100	0.8344	0.8301	0.8281	0.8267	0.8209
$K_1 \times 10^3$	158.85	160.51	163.09	165.72	167.89
$K_2 \times 10^3$	99.00	100.14	101.51	103.19	104.06
$K_3 \times 10^3$	−7.0	−7.3	−7.8	−12.0	−11.0

Contd.

Contd.

m	25°C	30°C	35°C	40°C	45°C
			30% dioxane + 70% water		
0	0.8185	0.8129	0.8073	0.8025	0.7992
0.003	0.8250	0.8202	0.8148	0.8080	0.8040
0.004	—	0.8215	0.8155	0.8094	0.8054
0.005	0.8276	0.8228	0.8165	0.8105	0.8065
0.006	0.8284	0.8238	0.8172	0.8114	—
0.007	0.8291	0.8239	0.8178	0.8120	0.8080
0.008	0.8298	0.8245	0.8183	0.8126	0.8085
0.009	0.8303	0.8249	—	0.8131	—
0.010	0.8307	0.8253	0.8191	0.8135	0.8094
0.020	0.8342	0.8277	0.8213	0.8161	0.8119
0.040	0.8357	0.8297	—	0.8183	0.8141
0.050	0.8364	0.8303	0.8237	0.8189	0.8147
0.060	0.8369	0.8308	0.8241	0.8194	0.8152
0.070	0.8374	0.8312	0.8244	0.8197	0.8156
0.080	0.8376	0.8314	0.8249	0.8201	0.8159
0.090	0.8379	0.8317	0.8250	0.8204	0.8161
0.100	0.8382	—	0.8252	0.8206	0.8–
$K_1 \times 10^6$	163.69	165.27	166.78	168.87	170.97
$K_2 \times 10^6$	99.59	100.46	101.22	102.40	103.50
$K_3 \times 10^4$	−10.0	−9.0	−8.5	−10.0	−10.0
			40% dioxane + 60% water		
0	0.8064	0.8018	0.7986	0.7928	0.7879
0.003	0.8140	0.8100	0.8052	0.7996	0.7940
0.004	0.8158	0.8114	0.8064	0.8009	0.7953
0.005	0.8168	0.8124	0.8075	0.8018	0.7962
0.006	0.8169	0.8131	0.8082	—	0.7969
0.007	0.8175	0.8148	0.8093	0.8032	0.7975
0.008	0.8180	0.8147	0.8094	0.8037	0.7980
0.009	0.8185	0.8151	0.8098	—	0.7985
0.010	0.8189	0.8175	0.8102	0.8045	0.7988
0.020	0.8212	0.8187	0.8125	0.8068	0.8011
0.040	0.8231	0.8195	0.8145	0.8087	0.8030
0.050	0.8236	0.8201	0.8150	0.8093	0.8035
0.060	0.8241	0.8205	0.8155	0.8098	0.8039
0.070	0.8245	0.8209	0.8159	0.8103	0.8043
0.080	—	0.8212	0.8161	0.8104	0.8046
0.090	—	0.8214	0.8163	0.8106	0.8048
$K_1 \times 10^6$	164.70	167.02	169.19	170.84	172.77
$K_2 \times 10^6$	98.02	99.26	100.23	101.18	102.06
$K_3 \times 10^4$	−8.5	−9.0	−9.0	−9.0	−9.0
			60% dioxane + 40% water		
0	0.7717	0.7677	0.7618	0.7587	0.7528
0.003	0.7850	0.7800	—	—	—
0.004	0.7870	0.7822	0.7775	0.7735	0.7687
0.005	0.7886	0.7839	0.7793	0.7752	0.7706
0.006	0.7899	0.7851	0.7807	0.7766	0.7721
0.007	0.7908	0.7862	0.7818	0.7777	0.7734
0.008	0.7917	0.7871	0.7871	0.7787	0.7744
0.009	0.7924	0.7878	0.7837	0.7795	—
0.010	—	0.7885	0.7844	0.7802	0.7760
0.020	0.7969	0.7947	0.7888	0.7846	0.7806
0.040	0.8002	0.7961	0.7927	0.7884	—
0.050	0.8013	0.7971	0.7938	0.7896	0.7861
0.060	0.8010	0.7979	0.7947	0.7904	0.7871
0.070	0.8025	0.7986	0.7955	0.7912	0.7878
0.080	0.8080	0.7992	0.7961	0.7918	0.7890
0.090	0.8084	0.7997	0.7966	0.7924	0.7893
0.100	0.8038	0.8001	—	0.7928	0.7897
$K_1 \times 10^6$	176.18	178.54	182.65	185.13	189.40
$K_2 \times 10^6$	96.06	97.23	98.57	99.67	101.02
$K_3 \times 10^4$	−15.0	−16.0	−18.0	−18.0	−20.0

The results of the transference number measured by Hittorf's method at concentrations 0.05, 0.08 and 0.10*M* at 25° are recorded in Table 3 together with the values found by e.m.f. method for comparison. The results were found to be in good agreement with each other.

TABLE 3—TRANSFERENCE NUMBER OF HCl AT 25°, DETERMINED BY E. M. F. AND HITTORF'S METHOD

Wt. % dioxane	10%	30%	40%	60%
		E. M. F. Method		
m				
0.05	0.8833	0.8864	0.8235	0.8010
0.08	0.8841	0.8876	—	0.8030
0.10	0.8844	0.8882	—	0.8040
Wt. % dioxane	10%	30%	40%	60%
		Hittorf's Method		
m				
0.05	0.8840	0.8862	0.8240	0.8018
0.08	0.8842	0.8872	—	0.8034
0.10	0.8848	0.8887	—	0.8047

It is known that the transference number vary with the concentration of the electrolyte and the following relationship[8] was verified to represent the variation :

$$t_+ = t_+^0 - Ac^{\frac{1}{2}} \qquad \ldots (6)$$

where t_+ and t_+^0 are the transference numbers of a given ion in a solution of concentration 'm' and at infinite dilution respectively ; 'A' is a constant and 'c' is the molar concentration corresponding to molality 'm' and was calculated from the density of the solution. A similar expression which holds good up to relatively high concentrations, is given by Jones and Dole[9] is :

$$\frac{t_+^0 + 1}{t_+ + 1} = 1 + Bc^{\frac{1}{2}} \qquad \ldots (7)$$

The two equations (equations 6 & 7) were used to determine the values of t_+^0 by suitable plots and the two t_+^0 values obtained by extrapolation were found to be in good agreement and the values for t_+^0 are reported in Table 2.

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Adsorption of Carbon Dioxide at 273°K on Hydrogels, Clay Minerals and Soils and Evaluation of Surface Area by Using Dubinin Equation

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Specific surface areas of a few microporous systems (hydrogels, clay minerals and soils) as obtained from (i) carbon dioxide adsorption isotherms (273°K) by applying Dubinin equation, (ii) nitrogen adsorption isotherms (77°K) by applying B.E.T. equation, (iii) water adsorption isotherms (298°K) by applying Harkins-Jura equation (in the case of hydrogels only), and (iv) glycol retension technique have been determined. The data indicate that while nitrogen molecules at 77°K can diffuse through the micropores in the case of hydrogels, they cannot do so effectively in the case of clays and soils. Carbon dioxide, due to its higher critical temperature, can be used at a much higher temperature and its molecules at 273°K seem to have sufficient kinetic energy to diffuse effectively in all cases except montmorillonite clays.

ADSORPTION of carbon dioxide at temperatures around 273°K has been used in recent years for estimating surface areas of a variety of carbons including coals[1-3], anthracites[4,5], activated carbons[6,7] carbon blacks[7,8] and carbon molecular sieves[6, 9] by applying Dubinin-Polanyi equation[10]. The widely used B.E.T. method is not regarded suitable in the case of microporous solids since adsorption of nitrogen at such a low temperature as 77°K is limited by activated diffusion of the gas through the micropores and an appreciable proportion of the internal surface remains inaccessible to the gas[11]. Carbon dioxide has a higher critical temperature (~ 304°K) and, therefore, can be used at a higher temperature. Anderson, Bayer and Hofer[11] have shown that a part of the internal surface in coals which is inaccessible to nitrogen at 77°K is accessible to carbon dioxide at 195°K even though molecular area of carbon dioxide (17 A°^{2}) is slightly higher than that of nitrogen (16.2 A°^{2}). Adsorption of carbon dioxide at 273°K is usually recommended. As the saturation vapour pressure (P_s) of carbon dioxide at this temperature is of the order of 34 atmospheres, the relative vapour pressure (P/P_s) along the isotherm remains very low. In this range of relative vapour pressure Dubinin-Polanyi (D-P) equation and not B.E.T. equation is applicable. The perusal of the literature shows that carbon dioxide adsorption at 273°K, as interpreted in the light of D-P equation, has not been used for estimating surface areas of hydrogels or clays and soils in all of which surface area is an important single value factor for their characterisation.

Experimental

Silica gel (N.C.L. Batch No. 0871), alumina gel (B.D.H.,C.P.), seven clay minerals received as gift from I.A.R.I., New Delhi through the courtesy of Dr. B. Ramamoorthy, and two soil samples were used in the present investigations. Adsorption of carbon dioxide (prepared by the action of dilute HCl (A.R.) on $CaCO_3$ (A.R.) and dried by passing through calcium chloride columns and of 99.8 per cent. purity) was studied volumetrically at 273°K, using a self-fabricated equipment after the well known B.E.T. apparatus. Equilibrium was attained within 40-45 min. at each pressure. Adsorption of nitrogen at 77°K was also determined on the same apparatus in the same manner. Liquid nitrogen was obtained from the Nangal Fertiliser Plant at Nangal. The saturation pressure (P_s) of CO_2 at 273°K was taken as 34.4 atmospheres while that of N_2 at 77°K was taken as 1 atmosphere. Adsorption of water vapour was studied at 298°K in the case of silica and alumina gels by using McBain's balance technique.

Specific surface areas were calculated by applying D-P equation to adsorption isotherms of carbon dioxide, and B.E.T. equation to adsorption isotherms of nitrogen. Surface areas of silica and alumina gels were also calculated from their water isotherms by using Harkins-Jura equation, as had been done by Orchiston[12] and Puri and Sharma[13]. Surface areas of soils and clays were also obtained by the glycol retension method proposed by Dyal and Hendricks[14] and used widely for this purpose in such systems.

Results and Discussion

According to D-P equation, which is intended to describe adsorption in microporous systems.

$$\log V = \log V_o - D(\log P_s/p)^2$$

where V is the volume of carbon dioxide adsorbed at equilibrium pressure P, V_o is micropore capacity, P_s is saturation pressure of the gas, and, $D=K/\beta^2$, where K is a constant at a given temperature while β is the affinity coefficient of the adsorbate.

The plots of $(\log P_s/p)^2$ against log V for some of the adsorbents, as shown in Figure 1, are linear,

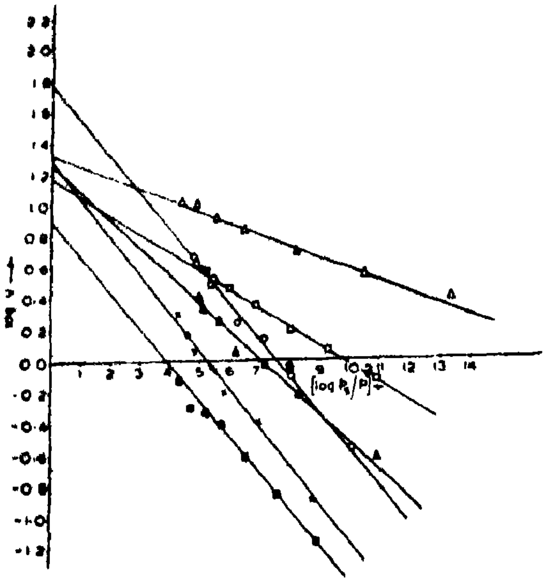


Fig. 1. Dubinin plots of CO_2 isotherms (273°K) on a few porous adsorbents (○—○ Silica gel, △—△ Alumina gel, ×—× Illite, □—□ Montmorillonite, ▲—▲ Halloysite, ■—■ Soil No. 2).

indicating applicability of the equation to our data. The plots for the rest of the samples were also similar and have not been given for reasons of space. The intercepts of the linear plots at $(\log P_s/P)^2=0$ give the respective values of V_o from which the respective surface areas could be calculated knowing the molecular area of carbon dioxide to be $17 A°^2$. This area may be taken as accessible to carbon dioxide molecules through pore entrances of width < 4.2 A° (molecular thickness of CO_2). The results are given in Table 1.

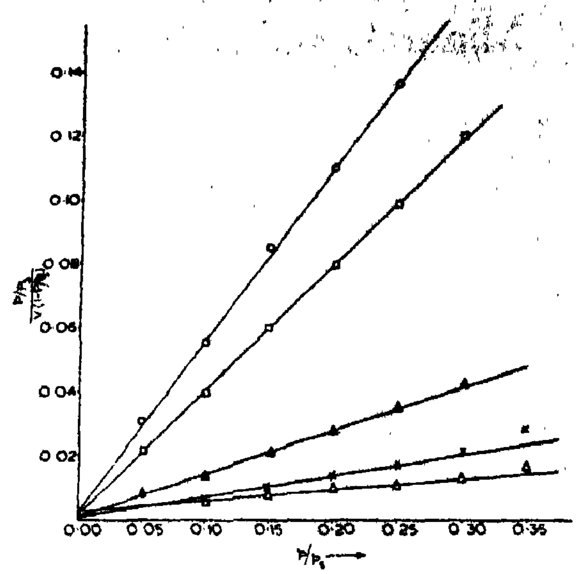


Fig. 2. B. E. T. plots for the adsorption of nitrogen (77°K) on a few porous adsorbents (△—△ Alumina gel, ×—× Illite, ▲—▲ Halloysite, □—□ Soil No. 2, ○—○ Vermiculite).

The B.E.T. plots of nitrogen at 77°K for some of the adsorbents are shown in Figure 2. The values of V_m, as obtained from the intercepts and slopes of these plots in the usual manner, and the surface area values calculated by taking molecular area of nitrogen as $16.2 A°^2$ are included in Table 1.

The Harkins-Jura plots for adsorption of water vapour at 298°K by silica and alumina gels are linear (Fig. 3), as expected. The values of surface area (S) obtained from the slopes (A) of the plots by employing the expression

$$S = K \times A^{\frac{1}{2}}$$

and taking the value of the constant K as 38.3[1a] are

TABLE—1 SURFACE AREAS OF POROUS ADSORBENTS AS OBTAINED BY DIFFERENT METHODS

Adsorbent	By adsorption of nitrogen (77°K ; B.E.T.)		By adsorption of CO_2 (273°K ; D-P) equation		By water adsorption isotherms (298°K)		By glycol retention method	
	V_m (cm³(STP)/g)	Surface area (m²/g)	V_o (cm³(STP)/g)	Surface area (m²/g)	Slope of H.J. plot	Surface area (m²/g)	Amount of glycol retained (mg/g)	Surface area (m²/g)
Silica gel	66.57	290	57.53	263	58.90	294	—	—
Alumina gel	28.56	124	20.35	93	10.99	127	—	—
Soil No. 1	1.38	6	5.91	27	—	—	8.1	26
Soil No. 2	2.60	11	7.87	36	—	—	12.4	40
Kaolin	6.43	28	7.44	34	—	—	9.8	30
Vermiculite	1.84	8	5.47	25	—	—	13.8	48
Illite	15.75	69	18.16	83	—	—	33.8	109
Pyrophyllite	1.15	5	9.68	44	—	—	18.0	58
Chlorite	1.15	5	5.91	27	—	—	13.3	43
Halloysite	7.49	33	17.94	82	—	—	32.9	106
Montmorillonite	4.14	18	14.44	66	—	—	79.4	256

also given in Table 1. The surface areas of clay minerals and soils obtained from glycol retention method are also included in the Table for easy comparison.

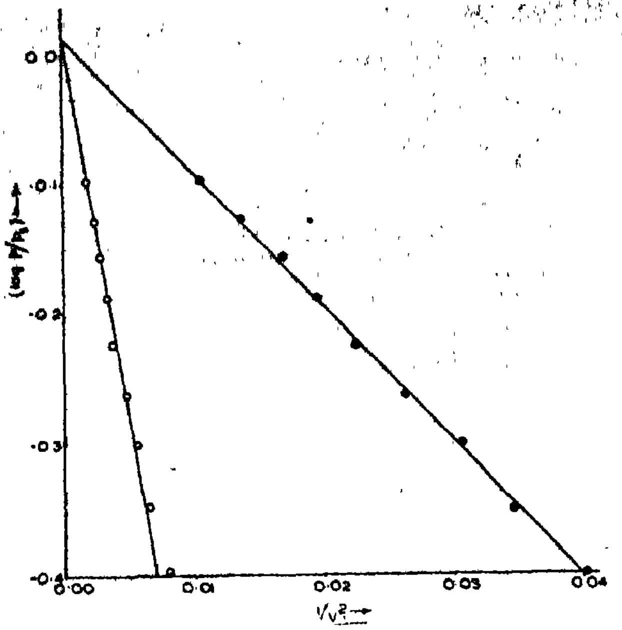


Fig. 8. Harkins-Jura plots for adsorption of water vapour (298°K) by Silica (O—O) and Alumina (●—●) gels.

It is seen, in the first place, that the values for silica and alumina gels, as obtained by the B.E.T. techuique, are fairly close to those obtained from water isotherms. As is well known these gels consist generally of open pores of cylindrical shape. It appears, therefore, that nitrogen molecules can diffuse through the system fairly well and most of the internal surface becomes accessible even at 77°K. The values obtained from the adsorption of carbon dioxide at the higher temperature of 273°K, by applying D-P equation, are, in fact, relatively smaller. This may be explained as due to slightly higher molecular area of carbon dioxide. In any case, the objection to the B.E.T. technique, on account of low rate of diffusion of nitrogen at 77°K, does not appear to be valid in the case of silica and alumina hydrogel systems.

As regards the soils and clay minerals, leaving montmorillonite aside for the present, it is seen that the CO_2 values are invariably higher than the nitrogen values. It appears that in these micro-porous systems, nitrogen at 77°K does not diffuse fully into the minute capillary pores while carbon dioxide at 273°K has sufficient kinetic energy to penetrate into them and hence a part of the surface inaccessible to nitrogen at the lower temperature becomes accessible to carbon dioxide at the higher temperature. The values obtained from glycol retention in the case of kaolin, which has an open structure, as well as the soils, are seen to be fairly close to those obtained from CO_2-isotherms. But in the case of the rest of the clay minerals, the values from glycol retention are comparatively higher. This may be, in part atleast, due to difference in the nature of forces involved. There may be some specific interaction of the hydrogen bonding type between —OH groups of glycol with the oxy- and oxy-hydrogen groups of soils and clays. In fact the method based on glycol retention may not be free from this possible objection. The use of carbon dioxide as an adsorbate at 273°K may provide a more suitable method for estimating surface areas of such systems.

It is in the case of montmorillonite that the carbon dioxide value, though appreciably higher than the nitrogen value, is considerably lower than the result obtained from the glycol retention method. Montmorillonite is an expanding lattice type of clay. When a substance like water, methanol or glycol enters between the ultimate sheets, it causes swelling and also separation of lamallae and therefore gets adsorbed and imbibed into the very interior of the system, as has been pointed out by Mooney, Keenan and Wood[15] as well as Nelson and Hendricks[16]. It is doubtful if a non-polar gas like carbon dioxide can diffuse through the very minute pores within the adhering sheets to give a complete coverage of the internal surface.

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Transannular Electronic Interaction of 1, 6-Cyclodecanedithione and Its Synthesis

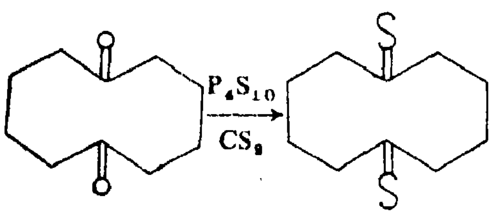
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An interesting ten-membered medium-sized ring compound, 1, 6-cyclodecanedithione, is prepared and its ultraviolet absorption spectra in carbon tetrachloride, tetrahydrofuran and chloroform are studied. The compound exhibits and unusual absorption bands at the wavelengths of 265 nm, 275 nm and 310 nm and have the molar absorptivities of 2657, 890 and 640 liter mole^{-1} cm^{-1} in carbon tetrachloride, tetrahydrofuran and chloroform respectively. The presence of a strong absorption band at 265 nm region is taken an evidence for this transannular electronic interaction in the excited state. The origin of $\pi \rightarrow \pi^*$ transition (K-band) and its assignment are discussed from the standpoint of the transannular electronic interaction (Transannular Conjugation)[1]. This is an interesting consequence of the stereochemistry of the ten-membered ring.

BY using naphthalene as starting material, a medium-sized ring compound, 1, 6-cyclodecanedione I, was prepared[2]. The dione I was next converted to 1, 6-cyclodecanedithione II by reacting it with phosphorus pentasulfide (Fig. 1). Some ketones have been changed to thioketones by the action of phosphorus pentasulfide[3].



I II

Fig. 1. Synthesis of 1, 6-Cyclodecanedithione

Sulfur and oxygen are both members of group IV of the periodic table. They have similar outer shell configuration and their chemistry is similar in part. Any differences in chemical behaviour may usually be attributed to the facts that sulfur is larger, less electronegative and has occupied 3p orbitals which are larger and higher in energy levels.

In contrast to oxygen, sulfur enters into p-p π bonding reluctantly when the reaction is forced upon it. The reasons for this reluctance of 3p orbitals to form π bonds are that the bonds are quite long, so that 3p overlap is not very effective. In the case of C=S group, the 2p-2p π bond, the 3p orbital occurs in such a way as to decrease the net effective overlap of the two orbitals. Therefore the 2p-3p π bond is weaker than the 2p-2p π bond. Thus thiocarbonyl compounds, in which the π bond of the C=S grouping is formed from overlap of the carbon 2p and sulfur 3p orbitals, are less stable than the corresponding carbonyl compounds and therefore easy to polarize with increase in solvent polarity.

The thiocarbonyl (C=S) group contains, in addition to a pair of σ electrons, a pair of π-electrons and two pairs of nonbonding (n or p) electrons on sulfur. The thioketones can give rise to two types of absorption bands, $\pi \rightarrow \pi^*$ transition and $n \rightarrow \pi^*$ transition. The short wavelength band is intense and arises from a $\pi \rightarrow \pi^*$ transition. The longer wavelength band is weak and arises from a $n \rightarrow \pi^*$ transition.

Transannular Interaction :

The ultraviolet and visible spectra of 1, 6-cyclodecanedithione have been measured in carbon tetrachloride and the compound exhibits an unusual absorption band at 265 nm with a molar absorptivity of 2657 liter mole^{-1} cm^{-1}. Similar bands have been observed in the spectra of other cyclic systems containing nonconjugated chromophores and have been attributed to transannular electronic interactions[2,4,5]. The presence of a strong absorption band in the 265 nm region is taken as evidence for this transannular electronic interaction in the excited state.

In the case of 1, 6-cyclodecanedithione, because of the flexibility and puckering of the ring, the nonconjugated two C=S chromophores can come closer to each other and assume a S-*cis*-butadiene type conjugation. This permits the orientation of the p-orbitals of the carbon and sulfur to be oriented parallel to each other and thus permit and effective overlap of the π-orbitals of the two C=S

chromophores (Fig. 2). This has been confirmed by the model construction. Such an orbital overlap gives rise to bonding and antibonding π-molecular orbitals which encompass both the chromophores.

Since thiocarbonyl compounds are polar, the positions of the K-bands and R-bands are both dependent on the solvent polarity. The K-bands ($\pi \rightarrow \pi^*$ transitions) of thioketones undergo a bathochromic shift (a red shift) and hypochromic effect with increasing solvent polarity. And R-bands ($n \rightarrow \pi^*$ transitions) of thioketones undergo a hypsochromic shift (a blue shift) as the polarity of the solvent is increased (Table I).

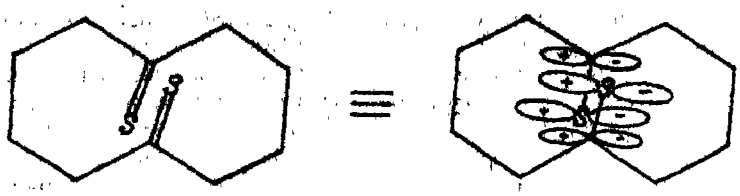


Fig. 2. π-Orbital Parellel Overlap.

Effect of Solvent Polarity :

In nonpolar solvent, carbon tetrachloride, the absorption band for two C=S chromophores of 1,6-cyclodecanedithione appears at 265 nm region. The 265 nm band can then be assigned to $\pi \rightarrow \pi^*$ transition (K-band). The strong K-band ($\pi \rightarrow \pi^*$ transition), $\epsilon m = 2675$, probably submerges the weak R-band ($n \rightarrow \pi^*$ transition).

When the spectra of 1,6-cyclodecanedithione was determined in tetrahydrofuran the absorption band appeared at the longer wavelength at 275 nm with molar absorptivity 890 liter $mole^{-1}cm^{-1}$. This absorption involves $\pi \rightarrow \pi^*$ transition in the C=S chromophores and undergoes a bathochromic shift (a red shift) as solvent polarity is increased. The red shift presumably results from a reduction in the energy level of the excited state accompanying dipole-dipole interaction. The weak absorption near 308 nm appears as a shoulder due to $n \rightarrow \pi^*$ transition (Table 1).

And when the spectra of 1,6-cylodecanedithione was determined in chloroform the absorption band appeared at 310 nm with molar absorptivity 640 liter $mole^{-1}$ cm^{-1}. This absorption involves an $\pi \rightarrow \pi^*$ transition in the C=S chromophores and undergoes a bathochromic shift as the solvent polarity is increased. The weak R-band due to $n \rightarrow \pi^*$ transition probably submerged under K-band due to the hypsochromic shift (a blue shift) of absorption to a shorter wavelength due to strong solvent effect.

TABLE—1 EFFECT OF SOLVENT POLARITY ON THE SPECTRUM OF 1,6-CYCLODECANEDITHIONE

Solvent	Transition $\pi \rightarrow \pi^*$ (λm, nm)	$n \rightarrow \pi^*$ (λm, nm)
Carbon tetrachloride	265	—
Tetrahydrofuran	275	308
Chloroform	310	Submerged under K-band

Similar effects of solvent polarity on the ultraviolet absorption spectra of mesityl oxide in isooctane, chloroform and water are observed[6].

Degree of Transannular Interactions :

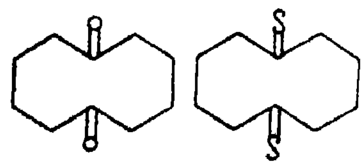
Four medium-sized ring compounds, 1,6-cyclodecanedione I, 1,6-dimethylenecyclodecane IV, 1,6-cyclodecanedione dioxime III and 1,6-cyclodecanedithione II have been synthesized and have been examined for evidence of C=O, C=C, C=N and C=S transannular interactions. These compounds I. II, III and IV exhibit different degrees of transannular interactions. 1,6-cyclodecanedione shows $\lambda m = 287$nm and $\epsilon = 35$; 1,6-dimethylenecyclodecane shows $\lambda m = 256$ nm and $\epsilon = 500$; cyclodecanedione dioxime shows $\lambda m = 246$ nm and $\epsilon = 13{,}200$;

TABLE—2 COMPARISON OF SPECTRAL DATA FOR 1,6-CYCLODECANEDITHIONE AND RELATED COMPOUNDS

Compound	Solvent	λm, nm	ϵ m
1,6-Cyclodecanedithione	Carbon tetrachloride	265	2,675
1,6-Dimethylenecyclodecane[8]	Ethanol	256	500
1,6-Cyclodecanedione Dioxime[8]	Ethanol	246	13,200
1,6-Cyclodecanedione[7]	Ethanol	287	35
Cyclodec-5-en-1-one[7]	Ethanol	258	472
1-Methyl-1-azacyclodecan-6-one[9]	Diethyl ether	221	5,600
1-Thiacyclooctan-5-one[4]	Carbon tetrachloride	238	2,535
1,5-Dithiacyclooctane[4]	Ethanol	202	3,000

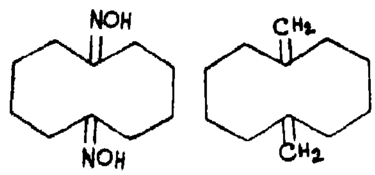
and 1,6-cyclodecanedithione shows λm = 265 nm and ε = 2675 (Table 2).

These compounds are chosen first because of the favourable geometry for such interactions of the ten-membered ring with diametrically opposed two similar functional groups and second to check the predicted correlation of the interactions of C=N>C=S>C=C>C=O order in the magnitude of the resulting ultraviolet absorption (Fig. 3).



I
λm = 287 nm
ε = 35

II
λm = 265 nm
ε = 2,675



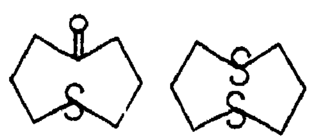
III
λm = 246 nm
ε = 13,200

IV
λm = 256 nm
ε = 500

Fig. 3. Transannular Interactions C=N > C=S > C=C > C=O

Transannular Interactions in Other Sulfur Compounds

Ultraviolet maxima of 1-thiacyclodecan-5-one V have been determined in carbon tetrachloride and the compound showed an unusual absorption band at 238 nm with a molar absorptivity of 2,565 liter/mole[4]/cm (Fig. 4). The interaction, in apparently nonconjugated system, is due to an effective overlap of the π-orbitals of the C=O group and the p (or n) orbitals of the sulfur[4] (Fig. 4).



V
λm = 238 nm
ε = 2565

VI
λm = 202 nm
ε = 3000

Fig. 4. Transannular Interactions in Related Sulfur Compounds.

Similar effects are observed when there can be effective overlap of the p (or n) orbitals of the two sulfur atoms across the ring of 1,5-dithiacyclooctane VI which showed strong absorption near 202 nm with molar absorptivity 300 liter/mole/cm[4] (Fig. 4).

Experimental

1,6-Cyclodecanedithione II :

Phosphorus pentasulfide (20 g) was dissolved in 100 ml carbon disulfide in a three-necked flask equipped with water condenser, separatory funnel and nitrogen inert atmosphere. Cyclodecanedione I (10 g) was dissolved in 100 ml carbon disulfide in a separatory funnel. The solution of cyclodecanedione was added slowly through separatory funnel to the solution of phosphorus pentasulfide. The reaction mixture was stirred under nitrogen atmosphere for seventy-two hours. Then water was added drop by drop to destroy the remaining phosphorus pentasulfide. The reaction mixture was poured into 1000 ml separatory funnel and the compound was extracted with carbon disulfide. The combined carbon disulfied extracts were dried over anhydrous magnesium sulfate overnight. It was filtered and the solvent was removed from the filtrate by rotary evaporator. The solid compound was recrystallized from carbon disulfide and was dried in vacuum oven. The yield was 80%.

The compound, 1,6-cyclodecanedithione, is insoluble in most of the organic solvents except carbon tetrachloride, tetrahydrofuran, chloroform and carbon disulfide. The melting point of the compound is 118° and is uncorrected. The infra-red absorption, for thiocarbonyl group (C=S) stretching frequencies, gives two sharp peaks at 1250 cm^{-1} and 1070 cm^{-1}. This is consistant with C=S absorption in thiourea and thiobenzophenone[9]. Ultra violet absorption spectra of the compound are at 265 nm in carbon tetrachloride ; 275 nm in tetrahydrofuran ; and 310 nm in chloroform. Carbon, sulfur and hydrogen analysis, calculated for $C_{10}S_2H_{16}$: C, 60% ; S, 32% ; H, 8%. Found : C, 60.08% ; S, 31.91% ; H, 8.05%.

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Synthesis in the 4-Azafluorene Group. Part III

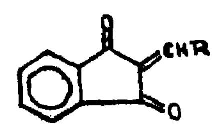
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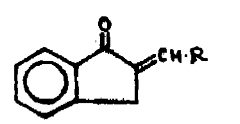
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The pyridine synthesis developed by Krohnke et al[1] have now been extended to the synthesis of 4-azafluorene and 4-azafluorenone. The limitations of the synthesis have been studied and alternative routs to the 4-azafluorene ring system have been explored. The fragmentation pattern of the mass spectrum of the 4-azafluorene (XIV) has been interpreted. A synthesis of 1-benzylideneindan-2-one is also described.

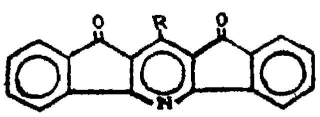
KROHNKE and coworkers[1] developed a novel synthesis of pyridines based on Michael addition of suitable pyridinium salts such as (VI-VIII) to α,β-unsaturated ketones using ammonium acetate as the source of nitrogen. When applied to benzylideneindan-1-one (IX) an elegant synthesis of 1, 3-diphenyl-4-azafluorene resulted. Since azafluorenones are known to be physiologically active[2], the experiments described in the present communication were carried out employing arylideneindan-1,3-diones (I-V)[2,3] with the ultimate end of studying the scope and limitations of the above synthesis.



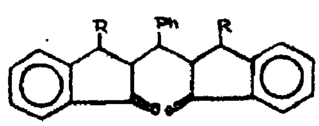
(I) $R=C_6H_5$
(II) $R=C_6H_4Me$ (*p*)
(III) $R=C_6H_4$ (OMe)(*o*)
(IV) $R=C_6H_4NO_2$ (*m*)
(V) $R=C_6H_4NO_2$ (*p*)
(VI) $PhCOCH_2PyBr$
(VII) CH_3COCH_2PyBr
(VIII) $CNCH_2PyCl$



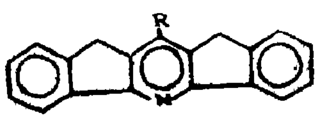
(IX) $R=C_6H_5$
(X) $R=C_6H_4NO_2$ (*o*)
(XI) $R=C_6H_4NO_2$ (*m*)



XII



XIII

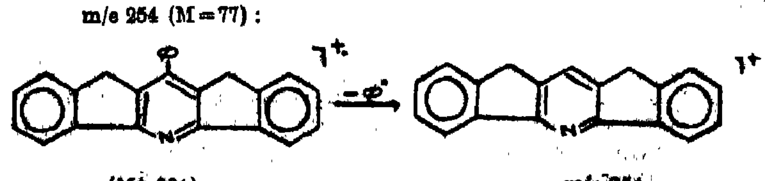


XIV

When arylideneindan-1,3-diones were treated with phenacylpyridinium bromide(VI) and ammonium acetate, the reaction took a different course giving the pentacyclic pyridines (XII) and surprisingly, the same result was obtained by using acetonylpyridinium bromide(VII) or cyanomethylpyridinium chloride (VIII). It was clear that a different reaction was taking place in preference and this could be traced to the dissociation and recombination of (I) to (XIII, R=O) and thence to (XII, R=Ph). This assumption was supported by the following facts: (i) Benzylideneindan-1, 3-dione (I) alone gave (XII, R=Ph) with ammonium acetate, (ii) benzylideneindan-1-one (IX) gave (XIV, R=Ph) with ammonium acetate and (iii) *bis*-benzylideneindan-1-one (XIII, R=2H) also gave (XIV, R=Ph) with ammonium acetate in good yield. Oxidation of (XIV, R=Ph) with chromic acid gave (XII, R=Ph) and Wolff-Kishner reduction of (XII, R=Ph) gave (XIV, R=Ph). The azafluorene (XIV) showed molecular ion peak at m/e 331 ($C_{25}H_{17}N$) followed by salient fragmentation ion peaks at m/e 254, m/e 253, m/e 241, m/e 165, m/e 164 and m/e 88. The formation of these ions may be rationalised according to the following scheme:

Our experiments however were more fruitful when we employed a modified Hantzsch[4] synthesis on (I) with β-phenyl-β-aminoacrylonitrile in acetic acid. The product (XVI), was aromatised (chromic acid) to (XVII), then hydrolysed to the acid (XVIII) and decarboxylated to the desired azafluorenone (XIX), The intermediate (XVII) could also be obtained by W-K reduction of (XVI) to (XXII) followed by chromic acid treatment. The azafluo-

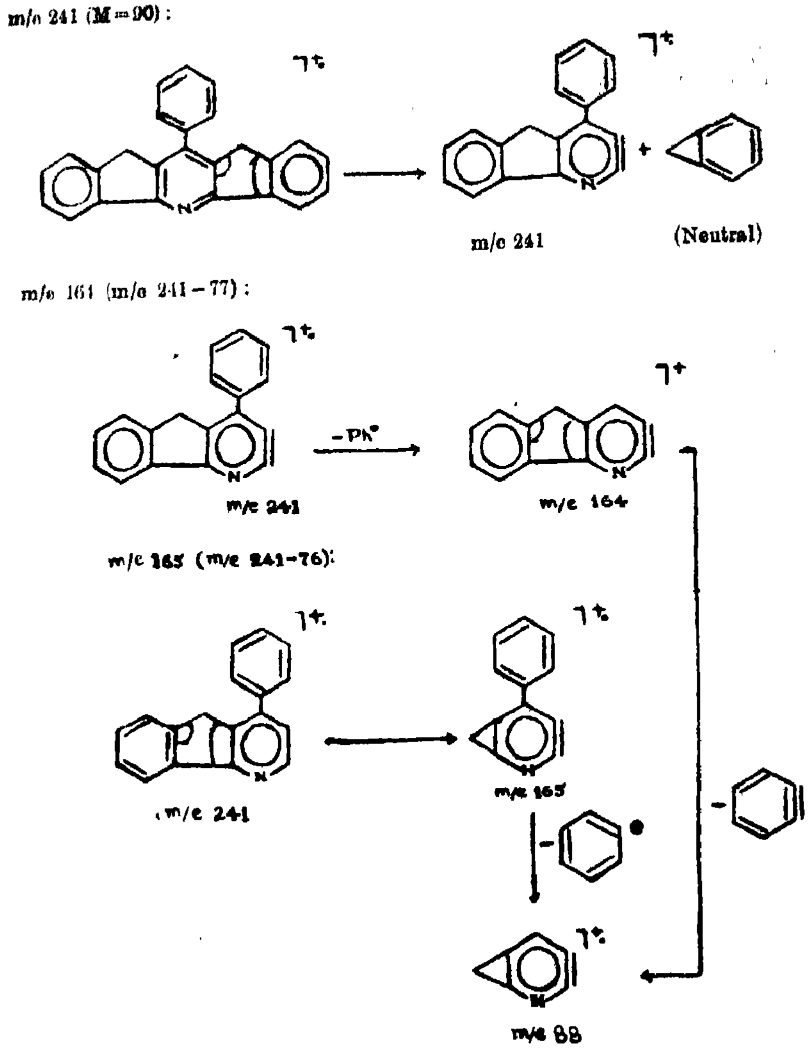
m/e 254 (M−77):



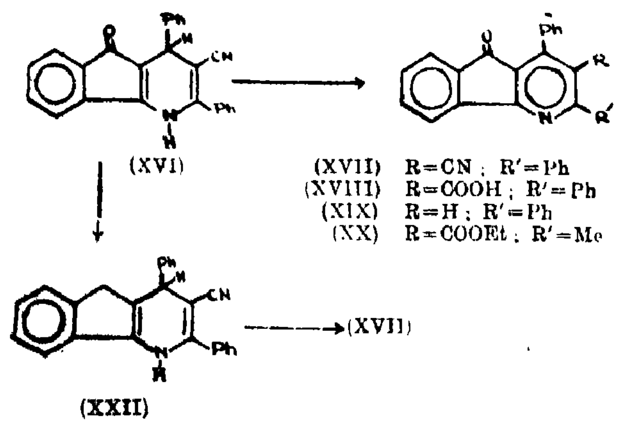
(M+ 331)

m/e 254
↓ −H°
m/e 253

m/e 241 (M−90):

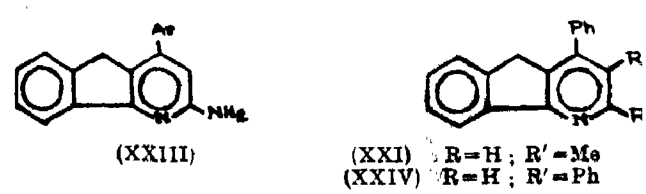


renone (XIX) on W-K reduction afforded the 1, 3-diphenyl-4-azafluorenone (XXIV).



$NH_2-C=CH-CN$
|
Ph

(XV)

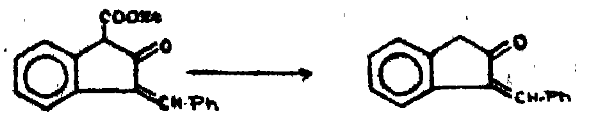


The cyanohydropyridine (XXII) was isolated in small quantity by a further adaptation of the foregoing Hantzsch[4] synthesis on benzylideneindan-1-one (IX) with (XV). Here again the main product was (XIV, R=Ph) (the aminonitrile was the obvious source of ammonia needed in its formation).

Benzylideneindan-1-one (IX) on treatment with acetonylpyridinium bromide (VII) and ammonium acetate gave 1-phenyl-3-methyl-4-azafluorene (XXI) along with (XIV, R=Ph). The structure of the former was established by its synthesis from the ester (XX) by hydrolysis, decarboxylation and

W-K reduction. This reduction was extended to o-methoxybenzylideneindan-1-one in a similar manner.

Reaction of arylideneindan-1-one with cyanomethylpyridinium chloride gave 1-aryl-3-amino-azafluorenes (XXIII).



XXV XXVI

1-Benzylideneindan-2-one (XXVI), hitherto unknown, and some 2-arylideneindan-1-ones have been reported by Harman *et. al*[4a]; may expected to give 1-azafluorene by ane xtension of the work adumbrated above. The compound has now been isolated from the known ester (XXV)[6] by hydrolysis and decarboxylation. Although preliminary experiments with pyridinium salts have not been encouraging, further experiments are underway to prepare 1-azafluorene and its derivatives.

Experimental

All melting points are uncorrected. The infra-red spectra were recorded in Perkin Elmer Infracord Model 237 Spectrophotometer.

Benzylideneindan-1-one (IX) :

A mixture of indan-1-one (0.7 g) and benzaldehyde (0.5 g) was dissolved in ethanol (8 ml) and conc. hydrochloric acid (5 drops) was added to it. The reaction mixture was refluxed on water bath for four hours, and the product, m. p. 110-11° (yield, 0.5 g) was identical with that prepared according to Mills and Akers[6] using zinc chloride as catalyst. (Found : C, 86.80 ; H, 5.75. Calc. for $C_{16}H_{12}O$: C, 87.24 ; H, 5.49%). The other substituted benzylideneindan-1-one were also prepared in the similar manner. *p*-Nitrobenzylideneindan-1-one (X) as yellow needles, m. p. 250-51°. (Found : C, 72.34 ; H, 5.21. $C_{16}H_{11}NO_3$ requires C, 72.44 : H, 4.18%) ; *m*-nitrobenzylideneindan-1-one (XI) as light yellow needles, m. p. 194-96°. (Found : C, 72.41 ; H, 4.94. $C_{16}H_{11}NO_3$ requires C, 72.44 ; H, 4.18%).

Attempted synthesis of 1,3-Diphenyl-4-azafluorenone (XIX) :

A mixture of 2-benzylideneindan-1, 3-dione (0.2 g), phenacylpyridinium bromide (VI, 0.225 g), ammonium acetate (0.62 g) and glacial acetic acid (20 ml) was allowed to reflux for two hours. The reaction mixture was then slowly cooled to room temperature when yellow crystals that separated were filtered and washed with water. The filtrate and the washings on further dilution gave a second crop of crystals. The product 2, 3, 5, 6-dibenzoylene-4-phenylpyridine was crystallised from pyridine methanol in yellow needles, m. p. 355-56° (yield, 90 mg) ; $\nu C{=}O$ 1720 cm^{-1}. (Found : C, 83.54 ; H, 3.69. $C_{25}H_{13}NO_2$ requires C, 83.56 ; H, 3.62%).

The dioxime was obtained as needles, m. p. 301-02°. (Found : C, 77.10 ; H, 4.12 ; N, 10.75. $C_{25}H_{15}N_3O_2$ requires C, 77.11 ; H, 3.88 ; N, 10.79%). Similarly prepared 2, 3, 5, 6-dibenzoylene-4-(2'-methoxyphenyl)pyridine (XII) was obtained as yellow needles, m. p. 320-21° ($\nu C{=}O$ 1710 cm^{-1}). (Found : C, 80.18 ; H, 3.91. $C_{26}H_{15}NO_3$ requires C, 80.20 ; H, 3.86%) ; 2, 3, 5, 6-dibenzoylene-4-(3'-nitrophenyl)pyridine as yellow needles, m. p. 365° ($\nu C{=}O$ 1710 cm^{-1}), (Found : C, 74.25 ; H, 3.35. $C_{25}H_{12}N_2O_4$ requires C, 74.25 ; H, 2.97%) ; 2, 3, 5, 6-dibenzoylene-4-(4'-nitrophenyl) pyridine as yellow needles, m. p. 360° ($\nu C{=}O$ 1712 cm^{-1}), (Found : C, 74.23 : H, 3.25. $C_{25}H_{12}N_2O_4$ requires C, 74.25 ; H, 2.97%) ; 2, 3, 5, 6-dibenzoylene-4-(4'-methylphenyl)pyridine as yellow needles, m. p. 360-61° ($\nu C{=}O$ 1710 cm^{-1}), (Found : C, 83.53 ; H, 4.04. $C_{26}H_{15}NO_2$ requires C, 83.63 ; H, 4.05%).

2,3,5,6-Dibenzylene-4.phenylpyridine (XIV,R=Ph) :

A mixture of 2-benzylideneindan-1,- one (IX ; 0.55 g), phenacylpyridinium bromide (0.7 g), ammonium acetate (2.0 g) and glacial acetic acid (3 ml) was allowed to reflux for two and half hours. The crystals of 2, 3, 5, 6-dibenzylene-4-phenylpyridine was filtered and crystallised from pyridine-methanol in colourless needles, m. p. 292-93° (Found : C, 90.57 ; H, 5.53. $C_{25}H_{17}N$ requires C, 90.60 ; H, 5.17%). Picrate, yellow needles, m. p. 265-66° (Found : C, 67.13 ; H, 2.55 ; N, 9.88. $C_{31}H_{14}N_4O_7$ requires C, 67.14 ; H, 2.52 ; N, 10.10%).

2, 3, 5, 6-Dibenzylene-4-phenylpyridine (XII) :

2, 3, 5, 6-Dibenzylene-4-phenylpyridine (0.1 g) in glacial acetic acid (4 ml) was treated with chromic acid (0.1 g) in a little water. The chromate of the base separated as an orange precipitate. The mixture was heated on water bath till the solution turned completely green (*ca.* 5 hours). The compound crystallised from pyridine-methanol in yellow needles, m. p. 356-57° ($\nu C{=}O$, 1720 cm^{-1}), (Found : C, 83.55 ; H, 3.68. $C_{25}H_{13}NO_2$ requires C, 83.56 : H, 3.62%).

The above compound (XII, 0.1 g) and hydrazine hydrate (100%, 4-5 drops) in ethylene glycol (5 ml) was heated on oil bath at 200° for 2-3 hours. On cooling (XIV, R=Ph) was obtained, m. p. 292-93° (yield, 0.06 g). (Found : C, 90.59 ; H, 5.20. $C_{25}H_{17}N$ requires C, 90.60 ; H, 5-17%).

1, 3-Diphenyl-4-azafluorenone-2-carboxylic Acid (XVIII) :

A mixture of 2-cyano-1, 3-diphenyl-4-azafluorenone (0.4 g) and hydrochloric acid (3 ml) was heated in a sealed tube at 160-70° for two hours. 1, 3-Diphenyl-4-azafluorenone-2-carboxylic acid separated from pyridine as brownish yellow needles, m. p.

212-14° (yield, 0.25 g) (νC=O 1708 cm^{-1}, ν COOH 1737 cm^{-1}). (Found : C, 79.48 ; H, 4.01. $C_{25}H_{15}NO_3$ requires C, 79.56 ; H, 40.01%).

1, 3-Diphenyl-4-azafluorenone (XIX) :

The foregoing acid (0.1 g) was heated carefully with Cu-bronze on a metal bath at 310-20° giving 1-3-diphenyl-4-azafluorenone which crystallised from pyridine-methanol in yellow needles, m. p. 169-70° (yield, 0.05 g) identical with an authentic specimen[1].

2-Cyano-1, 3-diphenyl-1, 4-dihydro-4-azafluorene (XXII) :

A mixture of 2-cyano-1, 3-diphenyl-1, 4-dihydro-4-azafluorenone (XVI), 0.2 g), hydrazine hydrate (100%, 2-3 drops) in ethylene glycol (3 ml) was heated in oil bath at 200° for two and half hours. The reaction mixture was then cooled and diluted with water. 2-Cyano-1, 3-diphenyl-1, 4-dihydro-4-azafluorene was collected, crystallised from benzene in dirty cream-coloured needles, m.p. 215-16°. (Found : C, 86.66 ; H, 5.42. $C_{25}H_{18}N_2$ requires C, 86.67 ; H, 5.24%).

2-Cyano-1, 3-diphenyl-4-azafluorenone (XVII) :

A solution of chromic acid (0.1 g) in a little water was added to a solution of 2-cyano-1, 3-diphenyl-1, 4-dihydro-4-azafluorene (0.1 g) in glacial acetic acid (4 ml). On working up 2-cyano-1, 3-diphenyl-4-azafluorenone crystallised from pyridine-methanol in cream-coloured needles, m.p. 274-75° (νC=O 1712 cm^{-1} ; νC=N, 2208 cm^{-1}). (Found : C, 83.75 ; H, 3.85 ; N, 7.70. Calc. for $C_{25}H_{14}N_2O$: C, 83.80 ; H, 3.91 ; N, 7.80%).

1,3-Diphenyl-4-azafluorene :

1, 3-Diphenyl-4-azafluorenone (XIX) (0.1 g) was mixed with hydrazine hydrate (100% ; 4-5 drops and ethylene glycol (3 ml) and heated in oil bath at 200° for three hours. The compound was obtained as colourless needles from pyridine-methanol, m. p. 158-59°. (Found : C, 90.25 ; H, 5.35. $C_{24}H_{17}N$ requires C, 90.25 ; H, 5.37%).

2-Cyano-1, 3-diphenyl-1, 4-dihydro-4-azafluorene (XXII) :

A mixture of benzylideneindan-1-one (IX, 0.2 g), β-phenyl-β-aminoacrylonitrile (XV, 0.14 g) and glacial acetic acid (2 ml) was refluxed for 4-5 hours. The reaction mixture was allowed to cool and set aside for two days. The product, m.p. 294-95° was identified as 2,3,5,6-dibenzylene-4-phenyl pyridine (XIV, R=Ph). The filtrate on dilution with water gave an oily compound which partly solidified on long standing. This was filtered and titurated with benzene to give (XXII) as cream-coloured needles, m.p. 212-14°. (Found: C, 86.65; H, 5.40. $C_{25}H_{18}N_2$ requires C, 86.67 ; H, 5.24%).

1-Phenyl-3-methyl-4-azafluorene (XXI)

A mixture of benzylideneindan-1- one (0.65 g), acetonyl-pyridinium bromide (VII, 0.6 g), ammonium acetate (1 g) and glacial acetic acid (4 ml) was refluxed for 3 to 4 hours and then worked up as usual. After removing (XIV, R=Ph), the filtrate was basified with sodium carbonate solution and then extracted with ether. 1-Phenyl-3-methyl-4-azafluorene (XXI, R=H ; R'=Me) was isolated as an oil and its picrate crystallised from glacial acetic acid in yellow needles, m.p. 232-33° (decomp.). (Found : C, 61.72 ; H, 4.01 ; N, 11.51, $C_{25}H_{18}N_4O_7$ requires C, 61.72 ; H, 3.72 ; N, 11.52%).

1-(2'-Methoxyphenyl)-3-methyl-4-azafluorene :

A mixture of *o*-methoxybenzylideneindan-1-one (0.625 g), acetonylpyridinium bromide (0.537 g), ammonium acetate (0-5 g) and glacial acetic acid (4 ml) was refluxed for 3-5 hours. The compound which separated was crystallised from pyridine-methanol in light yellow needles, m.p. 135-36°. (Found : C, 83.58 ; H, 6.21. $C_{20}H_{17}NO$ requires C, 83.59 ; H, 5.96%).

Ethyl 1-phenyl-3-methyl-1, 4-dihydro-4-azafluorenone carboxylate (XX, R=COOEt; R'=Me)

A solution of benzylideneindan-1, 3-dione (2.5 g) in glacial acetic acid (15 ml) was treated with ethyl β-amino crotonate (3 g) at boiling point. A deep red colour immediately developed, followed by separation of ethyl 1-phenyl-3-methyl-1, 4-dihydro-4-azafluorenone carboxylate (XX) which separated from acetic acid in dark red plates, m.p. 251-52°. (Found : C, 76.92 ; H, 4.95 ; $C_{22}H_{17}NO_3$ requires C, 76.93; H, 4.92%).

Ethyl 1-phenyl-3-methyl-4-azafluorenone-2-carboxylate :

The foregoing dihydro compound (XX, 0.2 g) was dissolved in warm acetic acid and treated with chromic acid (0.3 g) in water (2 ml). Ethyl 1-phenyl-3-methyl-4-azafluorenone-2-carboxylate crystallised from alcohol in lemon plates, m.p. 173-74° (νC=O 1720 cm^{-1} ; ν – COOEt 1735 cm^{-1}). (Found : C, 76.93 ; H, 5.45. $C_{22}H_{17}NO_3$ requires C, 76.95 ; H, 4.99%).

1-Phenyl-3-methyl-4-azafluorenone-2-carboxylic Acid :

The foregoing ester (0.2 g) was refluxed with 70% sulphuric acid (4 ml) at 160-80° for three hours giving 1-phenyl-3-methyl-4-azafluorenone-2-carboxylic acid which was obtained as needles from pyridine-methanol, m.p. 314-15° (decomp.). (Found : C, 76.18 ; H, 4.47. $C_{20}H_{13}NO_3$ requires C, 76.19 ; H, 4.16%).

1-Phenyl-3-methyl-4-azafluorenone :

A mixture of the foregoing acid (0.5 g), copper-

bronze (80 mg) and quinoline (4 ml) was refluxed for six hours. The azafluorenone crystallised from methanol in light yellow needles, m.p. 123-24° (νC=O 1712 cm^{-1}). (Found : C, 84.05 ; H, 4.92. $C_{19}H_{13}NO$ requires C, 84.11 ; H, 4.83%).

1-Phenyl-3-methyl-4-azafluorene (XXI, R=H ; R' =Me) :

A mixture of 1-phenyl-3-methyl-4-azafluorenone (0.1 g) and hydrazine hydrate (100% ; 0.5 c.c.) in ethylene glycol (4 ml) was heated at 180-90° for two hours and then at 225-30° for another one hour. The product (oil) gave a picrate which crystallised from acetic acid in yellow needles, m.p. 233-34° (decomp.). (Found : C, 61.72 ; H, 4.60 ; N, 11.43. $C_{25}H_{18}NO_7$ requires C. 61.73 ; H. 3.69 ; N, 11.55%).

1-(o-Methoxyphenyl)-3-amino-4-azafluorene (XXIII) :

A mixture of *o*-methoxybenzylideneindan-1-one (0.625 g), N-cyanomethylpyridinium chloride (0.40 g), ammonium acetate (1.5 g) and glacial acetic acid (4 ml) was refluxed for 3 hours. The product crystallised from pyridine in light yellow needles, m.p. 138-39°. (Found : C, 79.12 ; H, 6.01 ; $C_{19}H_{16}N_2O$ requires C, 79.14 ; H, 5.59%). Similarly, 1-(*m*-Nitrophenyl)-3-amino-4-azafluorene (XXIII) crystallised as light cream needles from pyridine, m.p., 199-201°. (Found : C, 71.25; H, 4.35. $C_{18}H_{13}N_3O_2$ requires C, 71.27 ; H, 4.32%).

Ethyl 3-benzylideneindan-2-one-1-carboxylate (XXV) :

It was prepared by the method of Scroth and Treibes[5] by condensing benzaldehyde with ethyl indan-2-one-1-carboxylate in the presence of 20% ethanolic potassium hydroxide.

Benzylideneindan-2-one :

Ethyl 3-benzylideneindan-2-one-1-carboxylate (0.1 g) was mixed with sulphuric acid (20% ; 2 ml) and heated on steam bath for nearly 2 and half hours. On cooling the reaction mixture was extracted with ether and treated with dilute sodium bicarbonate solution and the oily product distilled at 200°C/0.5 mm. (νC=0 1685 cm^{-1}). (Found : C, 87.24 ; H, 5.60. $C_{16}H_{12}O$ requires C, 87.24 ; H, 5.49%). The 2,4-dinitrophenyl hydrazone as yellow plates, m.p. 222-23° (decomp.). (Found : 65.98 ; H, 4.22. $C_{22}H_{16}N_4O_4$ requires C, 65.99 ; H, 4.03%).

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Synthesis of 8-Substituted-10, 11-Dihydro-11-Oxo-5H-Dibenzo (b, e) (1, 4) Diazepines : Part II

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Diazonium salt of 8-amino-10, 11-dihydro-11-oxo-5H-dibenzo (b, e) (1, 4) diazepine (1) was condensed with phenol, resorcinol α- and β-naphthols, 1-hydroxy-2-naphthoic and 3-hydroxy-2-naphthoic acids separately when azo dyes (2-7) were obtained. The structures of these azo dyes were established through elemental analysis and spectral studies. Colour reactions of these dyes have also been discussed.

DIBENZODIAZEPINES known as potent CNS drugs are used as antihistaminic, antiparkinson and neuroleptic drugs[1,2]. Tarpan[3], Noveril[4], Clozapine[5] are marketed drugs. Azo dyes are also important class of pharmacological drugs[6,7]. It was, therefore, thought to synthesize azo-derivatives of 8-amino-10, 11-dihydro-11-oxo-5H-dibenzo(b, e) (1, 4) diazepine (1)[8]. Diazonium salt of 1 was condensed at 0-5° with phenol, resorcinol, α- and β-naphthols 1-hydroxy-2-naphthoic and 3-hydroxy-2-naphthoic acids separately when corresponding azo dyes (2-7) with greenish yellow to orange shades were obtained.

Experimental

All the m. p's are uncorrected. Ir spectra were recorded on a Perkin-Elmer Infracord using KBr pellets. The purity of the compounds was ascertained by tlc using silica gel-G as stationary phase and C_6H_6 : C_2H_5OH : NH_3 (7 : 2 : 1-solvent layer) as mobile phase.

1-Hydroxy-4-[8-Azo-10, 11-Dihydro-11-Oxo-5H-Dibenzo(b, e) (1, 4) Diazepinyl] Benzene (2) :

To a diazotised solution of 1 (1.1250 g, 0.005 *M*, in 3 ml of conc. HCl, 2 ml of CH_3COOH and 0.4 g of $NaNO_2$ at 0-5°) alkaline solution of phenol (0.47 g in 5 ml of 10% NaOH) was gradually added with stirring. The precipitated dye was crystallised from ethanol (2, m. p. 270° d ; yield 1.010 g, .003 *M*, Rf. 0.60).

Analysis :

Found : C, 69.35 ; H, 4.42 ; N, 16.68 per cent.
Calcd. for : $C_{19}H_{14}O_2N_4$ (2)
C, 69.09 ; H, 4.24 ; N, 16.97 per cent.

On similar lines, the diazotised solution of 1 was condensed with resorcinol, α-naphthol, β-naphthol, 1-hydroxy-2-naphthoic acid and 3-hydroxy-2-naphthoic acid separately when the compounds 3-7 were obtained. The results of elemental analyses, melting points and yields of these dyes are compiled in Table 1.

Discussion

Azo dyes (2-7) gave blue to violet colour in acids (2 and 4-blue and 3, 5, 6 and 7-violet). On basification the colour of acidic solution of these dyes changed (2-brown ; 3-yellow ; 4-red ; 5-red ; 6-orange ; 7-red). The characteristic colour of these dyes in H_2SO_4 did not disappear even on boiling, these dyes were greenish yellow to orange in solid state changing to yellow in alcoholic solution. However, the alcoholic solution of 5 was red in colour.

The experimental values of elemental analyses were in agreement with the theoretical values as shown in Table 1.

Spectral Studies :

The absorption spectra of 2-7 were obtained in DMF and their λmax values alongwith molar extinc-

TABLE—1

Compound Number	Molecular formula	Melting point	Yield %	Rf	Analysis % Calculated C	H	N	Found C	H	N
2	$C_{19}H_{14}O_2N_4$	270°d	60.0	0.60	69.09	4.24	16.97	69.35	4.42	16.68
3	$C_{19}H_{14}O_3N_4$	279°d	57.80	0.72	65.90	4.05	16.18	65.55	4.55	16.38
4	$C_{23}H_{16}O_2N_4$	301°d	60.00	0.62	72.63	4.21	14.74	72.96	3.98	14.54
5	$C_{23}H_{16}O_2N_4$	291°d	63.16	0.54	72.63	4.21	14.74	72.98	3.90	14.56
6	$C_{24}H_{16}O_4N_4$	305°d	56.60	0.68	67.92	3.77	15.09	67.56	3.98	15.29
7	$C_{24}H_{16}O_4N_4$	309°d	57.55	0.64	67.92	3.77	15.09	67.58	4.02	15.33

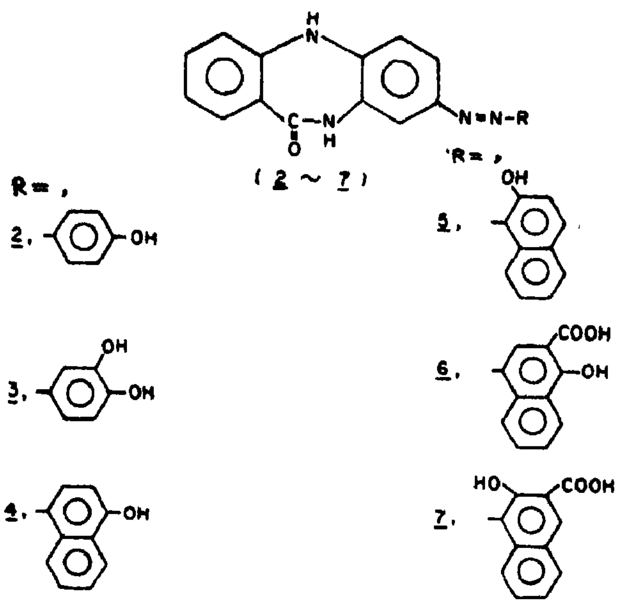
TABLE—2

Compound Number	Visible region λmax cm^{-1}	ε	Infra-red region Characteristic Absorption bonds cm^{-1}	Colour in Acid Medium	Colour in Alkaline Medium
2	412	12000	3565, 1640, 1580, 1405	Blue	Brown
3	455	12300	3565, 1650, 1575, 1395	Violet	Yellow
4	430	12065	3560, 1650, 1585, 1405	Blue	Red
5	475	13076	3560, 1645, 1575, 1380	Violet	Red
6	428	11904	3540, 1660, 1630, 1580 1395, 930, 1265	Violet	Orange
7	425	12698	3540, 1660, 1635, 1580, 1395, 1260, 935	Violet	Red

tion coefficient have been given in Table 2. These compounds were found to obey Beer's law.

Visible Absorption Spectra :

The absorption in the visible range was also studied. The values of λmax were found in the range 475-412 cm^{-1}. In the study of maximum absorption in visible range and visible colours, the range for compounds 2, 4, 6 and 7 which were yellow with greenish tinge was 430-400 cm^{-1}. λmax for 3 and 5 which were yellow with a little orange tinge were 455 cm^{-1} and 475 cm^{-1} respectively. The suggested range for such dyes (like 2 and 5) is 490-430 cm^{-1}.[9]



Infra-red Spectra :

The ir spectra of 1-7 were recorded in KBr pellets and were compared.

Although the ir spectra in the range of 1600-1100 cm^{-1} were quite complicated due to the presence of various groups and aromatic system but the absorption peaks in the vicinity of 1575 cm^{-1} and 1395 cm^{-1} appearing as side bands in the ir spectra of 2-7 were absent in the ir spectrum of 1 and these could be assigned to —N=N—stretching in these compounds. Strong absorption bands at 1660 cm^{-1} present in the ir spectra of 6 and 7 were absent in those of 1-5. The absorption bands also appeared in the vicinity of 1260 cm^{-1} aud 940-930 cm^{-1} in the ir spectra of 6 and 7 only. All these could be attributed to the presence of carboxyl group in 6 and 7.

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Carcinogenic Compounds : Synthesis of Polycyclic Carbazole Derivatives by Diels-Alder Reaction

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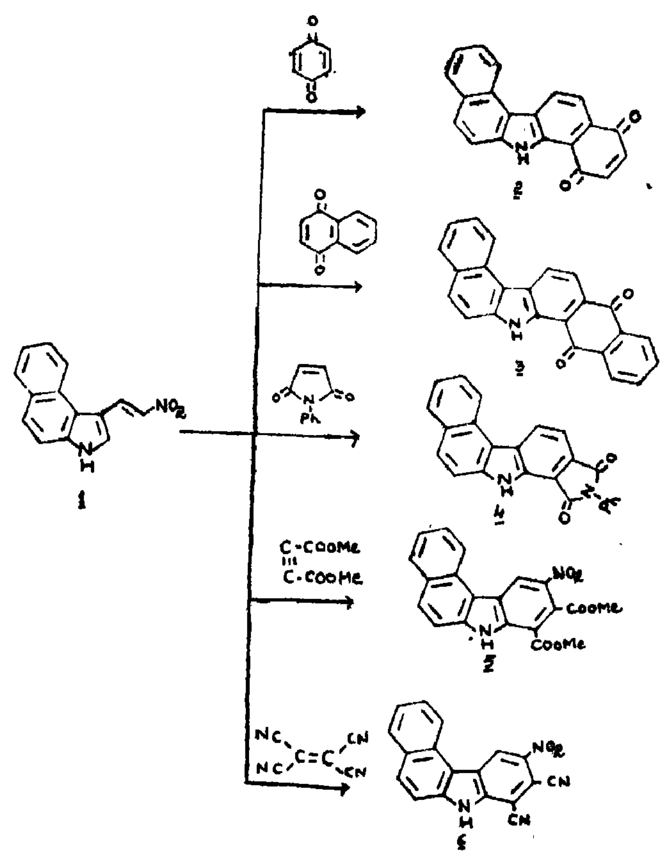
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The 3-(β-nitrovinyl)benz(e)indole (1) has been reacted with various dienophiles, 1,4-benzoquinone, 1,4-naphthoquinone, N-phenylmaleimide, dimethyl acetylenedicarboxylate and tetracyanoethylene, under the conditions of Diels-Alder reaction to yield the polycyclic benzocarbazoles.

IN recent years the polycyclic aromatic hydrocarbons have gained considerable interest owing to their carcinogenic properties. The carbazoles and benzocarbazoles, which have the structural similarity with polycyclic hydrocarbons, have also exhibited carcinogenic activity[1-5]. A few methods are available in the literature for the synthesis of such compounds. Amongst them the synthesis using Diels-Alder reaction conditions between vinylindoles[6] or nitrovinylindoles and dienophiles in polar solvents has been found to be most convenient. But the nitrovinylindoles are preferred to vinylindoles since the latter compounds are in most cases unstable and difficult to prepare. In our laboratory[7,8] several such carbazole derivatives have been synthesised employing nitrovinylindoles as the dienes. In view of these facts and in continuation of our work on benzindoles[9-11], we report here the synthesis of benzocarbazole derivatives.

The 3-(β-nitrovinyl)benz(e)indole[12] (*1*) was prepared from benz(e)indole-3-carboxaldehyde by a base-catalysed condensation with nitromethane. The nitrovinylindole was reacted with various dienophiles such as 1,4-benzoquinone, 1,4-naphthoquinone, N-phenylmaleimide, dimethyl acetylenedicarboxylate and tetracyanoethylene in dioxan under refluxing conditions. The appearance of a brownish gas in the formation of *2*, *3* and *4* immediately after the commencement of the reaction indicates that the condensation proceeded with the evolution of nitrous acid and its decomposed products. Simultaneously the aromatisation takes place—*via* a simple dehydrogenation to attain the ring stability. But in case of dimethyl acetylenedicarboxylate[7] and tetracyanoethylene[8] the Diels-Alder reaction took place without the evolution of brownish gas which indicates that in these cases the reaction proceeded with the retention of nitro group in the adduct.

The IR spectra of *2-4* exhibited bands at 3200 and around 1660 cm^{-1} due to NH and C=0 frequencies, respectively. The mass spectrum of com-



pound *3* exhibited the molecular ion peak at m/e 347(m$^+$, 100%), which confirms that aromatisation has taken place during the Diels-Alder reaction. Similar to the mass spectrum of benzoquinone, the peaks due to the favourable expulsion of CO from the molecular ion peak was observed at m/e 319 (m$^+$ – CO, 15.5%) and 291 (m$^+$ – 2CO, 18.2%). While studying the mass spectra of carbazoles, Riepe and

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Zander[13] have reported the elimination of H_2CN molecule from the carbazole moiety. In this case also the peak at m/e 263 [($m^+ - 2CO$) $- H_2CN$, 6.7%] may be due to the favourable expulsion of H_2CN molecule from ($m^+ - 2CO$) species. The peaks at m/e 348 ($m^+ + 1$, 40%) and 349 ($m^+ + 2$, 6.2%) may be due to the possible reduction of quinione to hydroquinone inside the heated inlet system of the spectrometer.

The ESR spectrum of the compound *2* has shown the expected 1 : 2 : 1 triplet. The free electrons from C=O of quinone have coupled with the adjacent proton of benzoquinone moiety to give rise to the above type of spectrum. This clearly indicates that the other part of the benzoquinone moiety has been fused with the diene (nitrovinyl system) to give *2*. In the caseof naphthoquinone adduct 3 the spectrum has shown a single peak, because the free electron of the anthraquinone system will have no scope for coupling with any protons as there are no protons in the ortho position. This confirms that in these cases the quinones have reacted with the diene in an usual Diels-Alder reaction fashion to give the expected adducts.

Experimental

The IR spectra were taken on a Perkin-Elmer Infracord and mass spectrum was recorded on AE1 MS 902 spectrometer at 70 eV. The ESR spectra were taken by capillary method in THF.

13H-Dibenzo(a,i)carbazole-1,4-quinone (2)

The 3-(β-nitrovinyl)benz(e)indole (0.71 g, 0.003 mole) was dissolved in dry dioxan (25 ml). 1,4-Benzoquinone (0.64 g, 0.006 mole) was added to it and the mixture heated under reflux for 48 h. The solution was concentrated (10 ml) and the brown solid that separated was filtered and washed with boiling petroleum ether (b.p. 60-80°) to remove any unreacted benzoquinone present. The compound *2* crystallised from dioxan as reddish brown needles (0.65 g, 0.0021 mole, 72%), m.p. 236° (Found : C,80. 5 ; H,3. 4 ; N,4.3 $C_{20}H_{11}NO_2$. Calc. C,80.8 ; H,3. 7 ; N,4.7%), νNH 3200w, νC=O 1650s, cm^{-1} in nujol.

8,9-Benzonaphtho(2,3-i)carbazole(5,13)quinone (3)

This compound was prepared from *1* and 1,4-naphthoquinone (0.94 g, 0.006 mole) following the procedure described for *2*. This crystallised from dioxan as pinkish shining needles (0.8 g, 0.0023 mole, 95%), m. p. 317° (Found : C, 82. 5 ; H, 3. 5 ; N, 4. 4 $C_{24}H_{13}NO_2$. Calc. C, 82. 9 ; H, 3. 7 ; N, 4. 4%), νNH 3200w, νC=O 1675s, cm^{-1} in nujol ; m/e 347 (m^+, 100%), m/e 319 ($m^+ - CO$, 15.5%), m/e 291 ($m^+ - 2CO$, 18.2%), m/e 263 [($m^+ - 2CO$) $- H_2CN$, 6.7%].

5,6-Benzocarbazole-1, 2-(N-phenyl)carboxamide (4)

This was prepared from *1* and N-phenylmaleimide (1 g, 0.006 mole) following the general procedure. The compound *4* crystallised from benzene as brown needles (0.6 g, 0.0026 mole, 89%), m. p. 145° (Found : C, 79.3 ; H, 3.4 ; N, 7.9 $C_{24}H_{14}N_2O_2$. Calc. C, 79.5 ; H, 3.8 ; N. 7.7%), νNH 3250w, νC=0 1720s, cm^{-1} in nujol.

Dimethyl 6-nitro-3,4-benzo-7, 8-dicarboxylate (5)

This was obtained from *1* and dimethyl acetylene dicarboxylate (0.85 g, 0.006 mole) following the general procedure, *5* Crystallised from benzene as brown needles (0.6 g, 0.0015 mole, 58%), m.p. 184° (Found : C, 63.5 ; H, 3. 8 ; N, 7. 6 $C_{20}H_{14}N_2O_6$. Calc. C, 63. 4 ; H, 3.7 ; N, 7.4%).

6-Nitro-8,9-dicyano-3,4-benzocarbazole (6)

A solution of *1* (0.71 g, 0.003 mole) and tetracyanoethylene (0.76 g, 0.006 mole) in dry benzene was kept at room temperature for 3 days. The solid that separated was filtered and washed with benzene. The compound *6* crystallised from dioxan as brown needles (0.65 g, 0.002 mole, 69%), m. p. 285° (Found : N, 17.5 ; $C_{18}H_8N_4O_2$. Calc. N, 17. 3%).

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Studies in the Cycloheptane Series. Part XXIX : Friedel-Crafts Reaction of the Anhydride of α,β-Diphenylglutaric Acid with Aromatic Hydrocarbons and Synthesis of Simple and Substituted Benz-2,3-diphenylcycloheptanes

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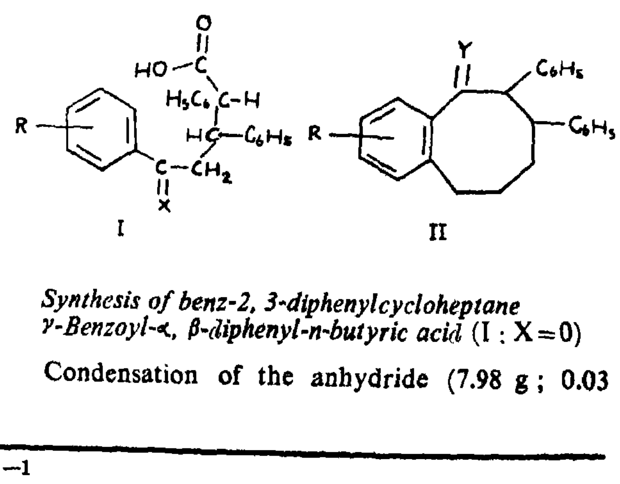
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The anhydride of α, β-diphenylglutaric acid is condensed with benzene, toluene, three isomeric xylenes, chlorobenzene and tetralin in the presence of anhydrous aluminium chloride and the corresponding γ-substituted aroyl-α,β-diphenyl-n-butyric acids have been obtained. These on Clemmensen reduction furnish the respective δ-aryl-α, β-diphenylvaleric acids which on cyclisation give the cyclic ketones. Clemmensen reduction of these give the simple and substituted benz-2, 3-diphenylcycloheptanes.

α, β-Diphenylglutaric acid, m. p. 230-31°, obtained by the hydrolysis of diethyl-α, β-diphenylglutarate, was convertedin to its anhydride, m. p. 125°. The latter on hydrolysis afforded the lower melting isomer (208-10°), which has a trans-configuration[1] and no attempts were made to separate the optical enantiomers. The anhydride of this lower melting acid, which also had the m. p. 125°[2], on condensation with benzene, toluene, isomeric xylenes, and chlorobenzene under Friedel-Crafts reaction conditions gave the corresponding keto-acids[3,4] (I : X=0). The structures of these were established by oxidation with sodium hypobromite to the known aromatic acids, m. ps. of which were undepressed by authentic samples.

Tetralin on similar condensation[5] yielded only γ-2-(5, 6, 7, 8-tetrahydronaphthoyl)-α, β-diphenyl-n-butyric acid (TLC).

Reduction of these keto-acids by modified Clemmensen method yielded the respective δ-aryl-α, β-diphenylvaleric acids (I : X = H_2). The identities of the acids (I : X=0 and X = H_2) were confirmed through elemental analysis, equivalent weight and characterisation made through I. R. spectral data and formation of S-benzylisothiuronium salts. The acids (I : X=0) gave doublets in the region 1690 cm^{-1} and 1710 cm^{-1} and acids (I : X = H_2) gave sharp peaks at 1690-1700 cm^{-1}. The acids (I : X = H_2) were cyclised with PPA to the corresponding cyclic ketones (II : Y=0), characterised through their 2, 4-DNPs and I. R. data (1700 cm^{-1}). Subsequent Clemmensen reduction of these yielded the simple and substituted benz-2, 3-diphenylcycloheptanes (II : Y = H_2).



I   II

Synthesis of benz-2, 3-diphenylcycloheptane

γ-Benzoyl-α, β-diphenyl-n-butyric acid (I : X=0)

Condensation of the anhydride (7.98 g ; 0.03

TABLE—1

γ-AROYL-α, β-DIPHENYL-n-BUTYRIC ACIDS

	Aroyl	m.p. °C	Molecular formula	Percentage Found C	Found H	Requires C	Requires H	S-Benzylisothiuronium salt m.p. °C
1.	4-Methylbenzoyl	177	$C_{24}H_{22}O_3$	80.8	5.8	80.4	6.0	104
2.	3, 4-Dimethylbenzoyl	174	$C_{25}H_{24}O_3$	80.5	6.4	80.6	6.4	110
3.	2, 4 " "	149	"	80.8	6.2	80.6	6.4	112
4.	2, 5 " "	194	"	80.6	6.8	80.6	6.4	106
5.	4-Chlorobenzoyl	152	$C_{23}H_{19}O_3Cl$	72.8	4.8	73.0	5.0	137
6.	2-(5, 6, 7, 8-Tetrahydronaphthoyl)	214	$C_{27}H_{26}O_3$	81.3	6.5	81.4	6.5	122

mole) with dry benzene (35 ml) and powdered anhydrous aluminium chloride (8.0 g ; 0.06 mole) and working up the reaction mixture in the normal manner gave the keto-acid (I ; X=0) (7.4 g ; 71.8%), m. p. 145-6° from benzene-pet. ether. (Found : C, 79.8 ; H, 5.8 ; equiv., 343.8. $C_{23}H_{20}O_3$ requires C, 80.0 ; H, 6.0% ; equiv., 344.0-monobasic).

Its *S-benzylisothiuronium salt* (shining plates) had m. p. 122°.

Other substituted butyric acids were similarly obtained in 70-80% yield and are entered in Table 1.

δ-Phenyl-α, β-diphenylvaleric acid (I : X=H_2)

The above keto-acid (6.88 g ; 0.02 mole) was reduced with zinc-amalgam (40 g) and concentrated hydrochloric acid (100 ml) (80 hr) ; on normal work up the acid (I ; X=H_2) was obtained in fine needles from benzene and had m. p. 177°. (Yield : 4.4 g ; 66.6%). (Found : C, 83.4 ; H, 6; 4. equiv., 329.8. $C_{23}H_{22}O_2$ requires C, 83.6 ; H, 6.4% ; equiv., 330-monobasic).

Its *S-benzylisothiuronium salt* (fine needles) had m. p. 112°.

All the other substituted valeric acids were obtained in 60-70% yield and are given in Table 2.

6, 7-Benz-2, 3-diphenylcycloheptan-1-one (II : Y=0)

The above acid (3.3 g ; 0.01 mole) was cyclised with PPA and the reaction product on working up gave the cyclic ketone (II : Y=0) from pet. ether (40-60°) in white cubes and had m.p. 164-5°, (Yield : 1.8 g ; 61.3%).

(Found : C, 88.3 ; H, 6.3. $C_{23}H_{20}O$ requires C, 88.5 ; H, 6.4%).

Its *2, 4-DNP* (cubes) had m. p. 233°.

All the other cyclic ketones similarly prepared in 60-65% yield are entered in Table 3.

6, 7-Benz-2, 3-diphenylcycloheptane

The above cyclic ketone (1.24 g ; 0.004 mole) on reduction with amalgamated mossy zinc (20 g),

TABLE 2

δ-ARYL-α, β-DIPHENYLVALERIC ACIDS

	Aryl	m.p. °C	Mol. formula	Percentage Found C	Found H	Requires C	Requires H	S-Benzylisothiuronium salt m.p. °C
1.	4-Methylphenyl	202	$C_{24}H_{24}O_2$	83.9	6.9	84.0	7.0	107
2.	3, 4-Dimethylphenyl	214	$C_{25}H_{26}O_2$	83.7	6.8	83.8	7.0	124
3.	2, 4- ,, ,,	204	,,	83.8	6.9	,,	,,	91
4.	2, 5- ,, ,,	208	,,	83.7	6.8	,,	,,	164
5.	4-Chlorophenyl	201	$C_{23}H_{21}O_2Cl$	73.8	5.5	74.0	5.7	162
6.	2-(5, 6, 7, 8-tetrahydro-naphthyl)	213	$C_{27}H_{28}O_2$	84.2	7.1	84.3	7.3	104

TABLE 3

SUBSTITUTED BENZ-2, 3-DIPHENYLCYCLOHEPTANE-1-ONES

	Substituents	m.p. °C	Mol. formula	Percentage Found C	Found H	Requires C	Requires H	2, 4-DNP m.p. °C
1.	8-Methylbenz	152	$C_{24}H_{22}O$	88.0	6.6	88.3	6.8	187
2.	7, 8-Dimethylbenz	165	$C_{25}H_{24}O$	88.1	8.2	88.2	8.4	230
3.	6, 8- ,, ,,	139	,,	88.0	8.4	,,	,,	225
4.	6, 9- ,, ,,	112	,,	88.1	8.3	,,	,,	141
5.	8-Chlorobenz	208	$C_{23}H_{19}OCl$	79.8	5.4	80.0	5.5	187
6.	7, 8-Tetramethylenebenz	270	$C_{27}H_{26}O$	88.4	6.9	88.5	7.1	141

TABLE 4

SUBSTITUTED BENZ-2, 3-DIPHENYLCYCLOHEPTANES

	Substituents	m.p.	Mol. formula	Percentage Found C	Found H	Requires C	Requires H
1.	8-Methyl	148	$C_{24}H_{24}$	92.1	7.6	92.3	7.7
2.	7, 8-Dimethyl	201	$C_{25}H_{26}$	91.8	8.0	92.0	8.0
3.	6 8- ,	137	,,	91.9	7.9	,	,,
4.	6, 9- ,,	143	,,	91.8	7.9	,,	,,
5.	8-Chloro	192	$C_{23}H_{21}Cl$	82.8	6.4	82.9	6.6
6.	7, 8-Tetramethylene	109	$C_{27}H_{28}$	91.8	7.9	92.0	8.0

concentrated hydrochloric acid (60 ml), toluene (1 ml) and glacial acetic acid (1 ml) (60 hr) furnished the hydrocarbon (II : $Y=H_2$) in fine cubes from benzene, m. p. 197° (Yield : 0.6 g ; 50%).

(Found : C, 92.4 ; H, 7.4. $C_{22}H_{22}$ requires C, 92.6 ; H, 7.4%.

All other hydrocarbons similarly prepared are entered in Table-4.

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Beckmann Rearrangement of the Oximes of 3-Aryl-4-Aroyl Butyric Acids and Synthesis of 3-(2′-Methoxy-5′-Methylphenyl)-4-Aminobutyric Acid

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A series of oximes of 3-aryl-4-aroyl butyric acids were synthesised which on Beckmann rearrangement gave corresponding N-aroyl-4-(2′-methoxy-5′-methylphenyl)-2-pyrrolidones. These pyrrolidones were then converted into 3-(2′-methoxy-5′-methylphenyl)-4-arylamido butyric acids. Drastic hydrolysis of these amido acids yielded 3-(2′-methoxy-5′-methylphenyl)-4-amino butyric acid.

IN view of the anti-inflammatory[1], herbicidal[2], antispasmodic[3] and analeptic[4] activities of N-aryl-2-pyrrolidones a series of N-aroyl-2-pyrrolidones (VI) were prepared. Identification of GABA as an important brain constituent[5] which act as an inhibitory neurotransmitter[6] to regulate CNS excitation[7] and its anticonvulsive activities[8] stimulated our additional interest to the hydrolytic transformation of these pyrrolidones to substituted GABA, 3-(2′-methoxy-5′-methylphenyl)-4-aminobutyric acid (VIII).

3-(2′-methoxy-5′-methylphenyl)-4-aroyl butyric acids[9] (Table 1)† on reaction with hydroxylamine hydrochloride in alkaline medium afforded the corresponding oximes (Table 2)††. The oximes (II) were characterised by elemental analysis and I.R. spectrum. '*syn*-aryl' configuration was assigned to these oximes on the basis of the product obtained after Beckmann rearrangement.

Beckmann rearrangement of the oximes using conc.

TABLE 1—M. P.S AND ANALYTICAL DATA OF 3-(2′-METHOXY-5′-METHYLPHENYL)-4-AROYL BUTYRIC ACIDS (I)

No	R_2	R_3	R_4^1	R_5	R_6	m.p.* °C	Yield** %	Molecular formula	C% Found	C% Required	H% Found	H% Req.
a	H	H	OAc	H	H	84-5	52	$C_{21}H_{24}O_5$	70.6	70.7	6.7	6.7
b	OMe	H	Me	H	OMe	92-3	57	$C_{22}H_{24}O_6$	68.2	68.3	6.8	6.7
c	Me	H	OAc	Prop	H	115-6	61	$C_{24}H_{28}O_5$	73.0	72.8	7.8	7.7

* All compounds were recrystallised from dilute acetic acid.
** Yields obtained by using Nitrobenzene as a solvent in Friedel-Crafts reactions.

TABLE 2—M.P.S AND ANALYTICAL DATA OF OXIMES OF 3-(2′-METHOXY-5′-METHYLPHENYL)-4-AROYLBUTYRIC ACIDS (II)

No	R_2	R_3	R_4	R_5	R_6	m.p.* °C	Yield %	Molecular formula	N% Found	N% Required
a	H	H	OAc	H	H	162-3	79	$C_{21}H_{23}NO_5$	3.6	3.7
b	Me	H	OMe	H	H	150-1	76	$C_{21}H_{25}NO_4$	3.8	3.7
c	OMe	H	H	Me	H	190-1	84	$C_{21}H_{25}NO_4$	3.6	3.7
d	OMe	H	Me	H	OMe	182-3	75	$C_{22}H_{27}NO_5$	3.4	3.4
e	Me	H	OMe	Prop	H	155-6	83	$C_{24}H_{31}NO_4$	3.1	3.3
f	Me	H	OAc	Prop	H	177-8	85	$C_{25}H_{31}NO_5$	3.2	3.2
g	H	H	OPh	H	H	179-80	78	$C_{25}H_{25}NO_4$	3.3	3.3

* All compounds were recrystallised from dilute ethanol.

† Other aroyl butyric acids are reported in literature (ref. 9).

†† Remaining 4 corresponding oximes are cited in literature (ref. 9).

H_2SO_4 gave dark resinous material while tosyl chloride gave back the unchanged oximes even under variety of conditions. Other acidic reagents such as phosphorus pentachloride and thionyl chloride were, therefore, employed but the highest yield was obtained using polyphosphoric acid. Migration of the 3-aryl butyric acid group to the nitrogen atom (*anti*-rearrangement) would result in the formation of III. This would eliminate a molecule of water, either directly to yield a azalactone (IV) or undergo a prototropic shift to V and then suffer a water loss to form the butyrolactam (VI) (Table 3). The butyrolactam structure was confirmed through its elemental analysis, I.R., N.M.R. and Mass spectra.

Mild hydrolysis of VI with ethanolic alkali yielded the amido acids (VII) (Table 4)-which on drastic hydrolysis gave two fragments, identified as 3-aryl-4-aminobutyric acid (VIII) and anisic acid (IX). The hydrolysis of VII was not affected even with conc. HCl or H_2SO_4.

The various substituents $-OCH_3$, $-OC_2H_5$, etc., on the aryl nucleus had no effect on the course of the Beckmann rearrangement as the nature of the products of the *anti*-rearrangement and products of hydrolysis was the same in all cases.

Pyrrolidones(VI) have shown promising *anti*-inflammatory activity while the pharmacological evaluation of GABA (VIII) is in progress.

Experimental

Melting points were recorded on a Gallen-Kamp melting point apparatus and are uncorrected. I.R. spectra were recorded on a Perkin-Elmer infrachord or Beckmann I.R. spectro photometer. N.M.R. spectra were recorded on a Varian A-60 spectrometer with tetramethyl silane (TMS) as an internal standard. Mass spectra were recorded with a CH-7 Varian Mass spectrometer. The ionizing voltage was 70 e.v. and the ion source temperature 150°.

Oxime (IIa) of 3-(2'methoxy-5'-methylphenyl)-4-(4'-methoxybenzoyl) butyric acid (Ia) :

3.39 g (0.01 m) of keto acid (Ia) was dissolved in lN NaOH solution (20 ml). This was heated on a water bath with 0.735 g (0.01057 m) of hydroxylamine hydrochloride for about 30 min. Reaction mixture on cooling was acidified with dilute acidic acid to separate solid mass which was washed with water and crystallised from dil. ethanol in greenish needles (3.03 g), m.p. 172°, tlc 3 : 2 chloroform-ethylacetate. ir (KBr) : γmax. 3150—2850 (–OH), 1700 (C=O of carboxylic group), 1640 (C=N) and 945 (N—O—) cm^{-1}.

Similar procedure has been adopted for the other oximes listed in Table 2.

N-(4'-methoxybenzoyl)-4-(2'-methoxy-5'-methylphenyl)-2-pyrrolidone (VIa) :

TABLE 3—M.P.S AND ANALYTICAL DATA OF N-AROYL-4-(2'-METHOXY-5'-METHYLPHENYL)-2-PYRROLIDONES (VI)

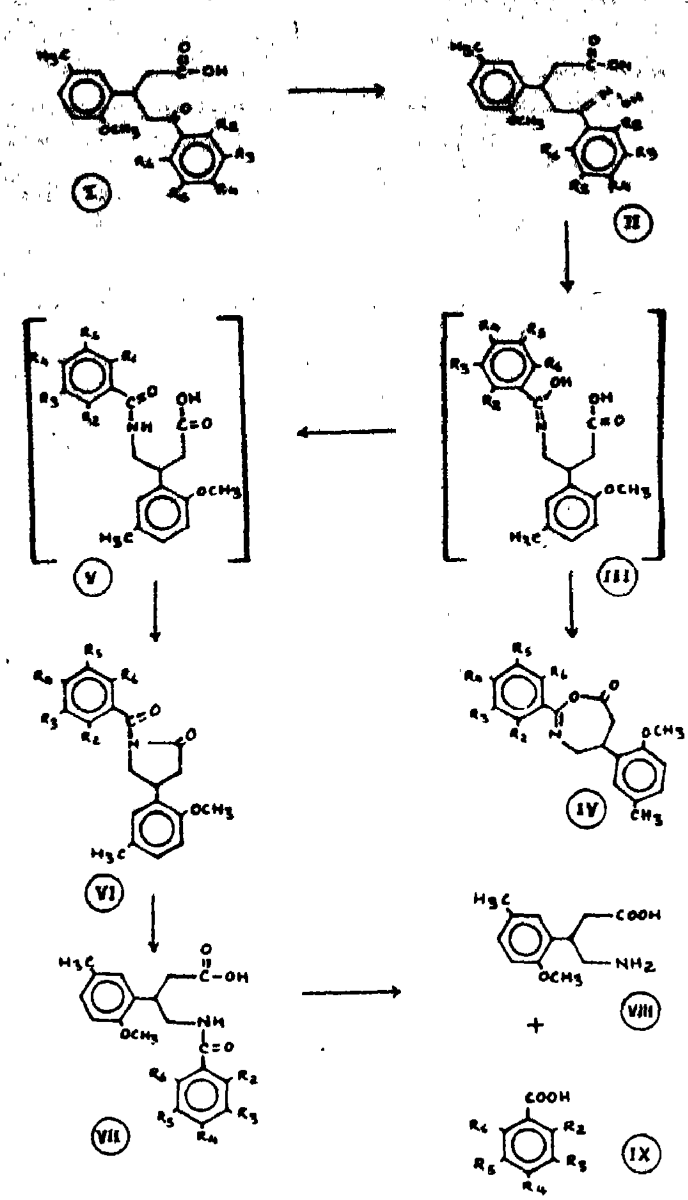
No	R_2	R_3	R_4	R_5	R_6	m.p.* °C	Yield** %	Molecular formula	N% Found	N% Required
a	H	H	OMe	H	H	165-6	70	$C_{20}H_{21}NO_4$	4.1	4.1
b	H	H	OAc	H	H	120-1	62	$C_{21}H_{21}NO_4$	3.8	3.9
c	H	Me	OMe	H	H	158-9	55	$C_{21}H_{23}NO_4$	4.0	3.9
d	Me	H	OMe	H	H	129-30	65	$C_{21}H_{23}NO_4$	3.8	3.9
e	OMe	H	H	Me	H	120-1	58	$C_{21}H_{23}NO_5$	4.0	3.9
f	OMe	H	OMe	H	H	148-9	66	$C_{21}H_{23}NO_5$	3.6	3.7
g	OMe	H	H	OMe	H	161-2	69	$C_{21}H_{23}NO_5$	3.6	3.7
h	OMe	H	Me	H	OMe	158-9	60	$C_{22}H_{25}NO_5$	3.7	3.6
i	Me	H	OMe	Prop	H	138-9	54	$C_{24}H_{29}NO_4$	3.4	3.5
j	Me	H	OAc	Prop	H	166-7	59	$C_{25}H_{29}NO_5$	3.5	3.4
k	H	H	OPh	H	H	169-70	68	$C_{25}H_{23}NO_4$	3.5	3.4

* All compounds were recrystallised from ethanol.
** The yields obtained using PPA.

TABLE 4—M.P.S AND ANALYTICAL DATA OF 3-(2' METHOXY-5'-METHYLPHENYL)-4-ARYLAMIDOBUTYRIC ACIDS (VIII)

No	R_2	R_3	R_4	R_5	R_6	m.p.* °C	Yield %	Molecular formula	N% Found	N% Required
a	H	H	OMe	H	H	162-3	65	$C_{20}H_{23}NO_5$	3.9	3.9
b	H	H	OAc	H	H	171-3	62	$C_{21}H_{23}NO_6$	3.7	3.8
c	H	Me	OMe	H	H	191-2	49	$C_{21}H_{25}NO_5$	3.7	3.7
d	Me	H	OMe	H	H	194-5	52	$C_{21}H_{25}NO_5$	3.7	3.8
e	OMe	H	H	Me	H	162-3	48	$C_{21}H_{25}NO_5$	3.7	3.8
f	OMe	H	OMe	H	H	182-3	55	$C_{21}H_{25}NO_6$	3.7	3.8
g	OMe	H	H	OMe	H	201-2	61	$C_{21}H_{25}NO_6$	3.7	3.6
h	OMe	H	Me	H	OMe	210-2	42	$C_{21}H_{25}NO_6$	3.6	3.6
i	Me	H	OMe	n-Prop	H	186-7	49	$C_{23}H_{27}NO_5$	3.4	3.3
j	Me	H	OAc	n-Prop	H	198-9	51	$C_{24}H_{31}NO_6$	3.4	3.3
k	H	H	OPh	H	H	172-3	62	$C_{25}H_{25}NO_5$	3.2	[illegible]
								$C_{25}H_{25}NO_5$	3.3	3.2

* All compounds were recrystallised from dilute ethanol. Satisfactory C,H analysis have been obtained for all the compounds.



(i) Using Phosphorus pentachloride—

1.8 g of phosphorus pentachloride (0.0086 m) was added in small portions to the well stirred solution of 3.57 g (0.01 m) of oxime (II) dissolved in dry tetrahydrofuran (50 ml) at ice-cooled and moisture free conditions. The solution was left overnight at room temperature. The separated solid was filtered, dried and crystallised from absolute ethanol to give 2 g yellowish needles (58% yield), m.p. 165-6°.

(ii) Using Thionyl Chloride—

To a well shaken suspension of 3.57 g (0.01 m) of oxime (II) in chloroform (35 ml), was added 1.7 ml thionyl chloride (0.0226 m) gradually at 30-35° and the reaction mixture was left at the same temperature for four hours. The sticky mass obtained on removal of the solvent solidified on trituration with methanol. The solid on crystallisation from absolute ethanol afforded 2.1 g yellow needles (62% yield), m.p. 165-6°.

(iii) Using Polyphosphoric acid—

3.57 g (0.01 m) of oxime(II) was heated with 8 ml of PPA (5 : 3 of P_2O_5 and orthophosphoric acid) for 8 hours on a water bath. On cooling to room-temperature the reaction mixture was poured in crushed ice with continuous stirring, when a solid was separated. The residue was chromatographed on silica gel. Elution of the column with Benzene-Methanol (5 : 1) gave the required pyrrolidone which was recrystallised from ethanol in pale yellow needles (2.37 g), m.p. 165-6°. ir (KBr) : νmax. 1735 (C=O of five membered ring) and 1685 (C=O of tert. amido gr.) cm^{-1}, nmr δ ($CDCl_3$) 1.2 (s, 1,CH), 2.25 (s,3,ArCH_3), 2.55 (d,2,COCH_2), 3.2 (d,2,NCH_2), 3.8 (s,6,OCH_3) and 7.0 (m,7, ArH). Mass : M$^+$ m/e 339. Adopting the identical conditions, other compounds of the type VI (Table 3) have been synthesised.

3-(2'-methoxy-5'-methylphenyl)-4-(4'-methoxybenzamido) butyric acid (VIIa) :

1.69 g (0.005 m) pyrrolidone (VIa) was refluxed with 1*N* ethanolic NaOH (30 ml) for 6 hours. The excess of ethanol was distilled off and residue dissolved in water and acidified with dil. HCl to give a solid which was crystallised from dil. ethanol, m.p. 162-3°, tlc 4 : 1 Benzene-Ethylacetate.

ir (KBr) : ν max. 2950-2700 (–OH of carboxylic group), 3350 (NH), 1700 (C=O of carboxylic group), 1680 1590 1260 (amide I, II and III resp.) cm^{-1}. nmr δ ($CDCl_3$) 1.2 (s,1, CH), 2.25 (s,3, ArCH_3), 2.85 (d,2, NCH_2), 2.95 (d,2, CH_2), 3.8 (s,6, OCH_3), 7.0 (m,7, ArH), 7.7 (s,1, NH collapsed on D_2O exchange) and 11.0 (s,1, COOH collapsed on D_2O exchange).

Mass : M$^+$ m/e 357.

Other amido acids (VIIa-1) were obtained by following the similar procedure and are listed in Table 4.

3-(2'-methoxy-5'-methylphenyl)-4-aminobutyric acid (VIII)—

1.78 g (0.005 ml) amido acid (VIIa) was dissolved in 10*N* aq. NaOH (25 ml) and refluxed for 8 hrs. The content was cooled and acidified with dil. HCl and the solid thus obtained was passed through a column having silica gel as adsorbant, benzene-chloroform (1 : 1) as eluent and was recrystallised from dil. ethanol in pale yellow crystals, m.p. 154-5°.

Anal. Found : C, 63.11 ; H, 7.20 and N, 6.65%.

Calcd. for $C_{12}H_{18}NO_3$; C, 63.06 ; H, 7.17 and N, 6.69%.

ir (KBr) : showed that the amino acid exist in the form of Zwitter ion and the main absorptions are those arising from amine hydrochloride and carboxylate ion. ν 3010 2870 2600 2310 (prim. amine salt), 1610 (NH_3^+ asym. bending), 1600 (COO^- asym. stretching), 1500 (NH_3^+ sym. bending), 1410 (COO^-

sym. stretching) and 1235 1125 (NH_3^+ rocking) cm^{-1}. nmr δ (CF_3COOH) 1.1 (s, 1, CH), 1.7 (s, 3, $ArCH_3$), two-CH_2 protons form a complex pattern with $-NH_3^+$ protons in the region 2.5-3.3 (s, 3, OCH_3) and 6.4 (m, 3, ArH).

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Studies on N-substituted 3 : 5-Dihalo Propesin Derivatives as Potential Local Anesthetics

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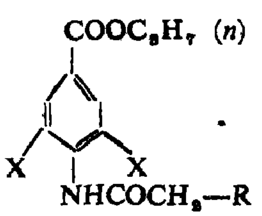
Potential local anesthetics of the type :

$$C_6H_2X_2 < \begin{matrix} COOC_3H_7\ (n) \\ NHCOCH_2R \end{matrix}$$

where X is Br or I and R is from different amines, have been prepared. The free bases have been converted into their hydrochlorides and some of them have been tested for their local anesthetic activity.

ESTERS of *p*-aminobenzoic acid are known for their local anesthetic activity[1]. It has been reported that local anesthetic activity increases with increasing the number of carbon atoms of ester group and is highest in Butyl *p*-aminobenzoate[2].

In continuation of our previous work[3], we have prepared N-substituted 3 : 5-dibromo/diiodo propesin derivatives of the type,



where X is Br or I and R is alkyl, aryl, heterocyclic or alicyclic amino moiety. The compounds have been prepared by chloroacetylation of 3, 5-dibromo propesin or 3, 5-diiodo propesin and then condensation with various amines.

The free bases are converted into their hydrochlorides by passing dry HCl gas in the ethereal solution. Some of them have been investigated for their local anesthetic activity. They have been tested for surface anesthesia by corneal block method of Chance and Lobstein[4] and for intradermal anesthesia following the method of Parel[5] on guinea-pig. The activity was compared with cocaine. HCl, procaine. HCl and lignocaine. HCl. The results recorded in Table 2 indicate that the compounds show better intradermal anesthetic activity rather than surface anesthetic activity. Preliminary studies prove that they are better than procaine because they have activity equal to that of procaine with longer duration of local anesthetic action. In surface anesthesia, two out of three have activity equal to that of lignocaine with almost equal duration of action.

IR Spectra :

The IR spectra have been recorded on Beckmann IR-5 spectrophotometer at the Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar in nujol as mulling agent. Bands are observed as follows for 3, 5-dibromo propesin at (approx.) 3450, 3400, 3100, 2915, 2870, 1730, 1685 1600, 1555, 1500, 1460, 1380, 1315, 1290, 1245 and, 890 cm^{-1}.

For 3, 5-diiodo propesin at (approx.) 3450, 3400, 3140, 2910, 2875, 1730, 1675, 1600, 1560, 1520, 1460, 1380, 1310, 1275, 1240 and 895 cm^{-1}.

For N-chloroacetyl-3, 5-diiodo propesin at (approx.) 3175, 2920, 2868, 1730, 1670, 1565, 1515, 1460, 1382, 1320, 1280, 1245, 890 and 758 cm^{-1}.

For N-chloroacetyl-3, 5-dibromo propesin at (approx.) 3205, 2918, 2865, 1725, 1680, 1562, 1510, 1465, 1385, 1315, 1280, 1242, 885 and 760 cm^{-1}.

For N-morpholinoacetyl-3, 5-dibromopropesin at (approx.) 2915, 2870, 1930, 1675, 1555, 1460, 1380, 1315, 1290, 1260, 1240, 1115, 1020, 980, 865, 762 and 735 cm^{-1}.

For N-benzylaminoacetyl-3, 5-dibromo propesin at (approx.) 3310, 3245, 2925, 2875, 1730, 1690, 1520, 1460, 1380, 1560, 1515, 1275, 1245, 1195, 1140, 1125, 975, 760, 740 and 700 cm^{-1}.

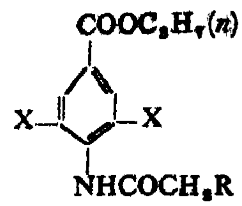
Experimental

Preparation of 3, 5-dibromo propesin :

Propesin (0.1 *M*) was dissolved in glacial acetic acid (50 ml) and bromine (0.25 *M*) in glacial acetic acid (50 ml) was added slowly with constant stirring at 0°. The product separated immediately which was filtered, dried and recrystallised from ethanol in long needles, m. p. 84° (62-4.4° is reported by Wells[6]).

TABLE—1

COMPOUNDS OF THE TYPE

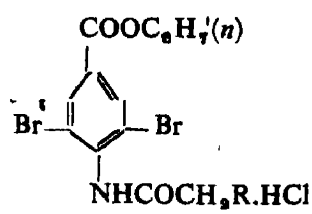


Sl. No. (1)	R (2)	X (3)	Molecular Formula (4)	m.p.°C (5)	% N (6) Requd.	% N (6) Found	% Br (7) Requd.	% Br (7) Found
1	n-C_4H_9NH	Br	$C_{16}H_{22}Br_2N_2O_3$	* 84 200	6.22	6.36	41.02	41.06
2	$C_6H_5CH_2NH$	Br	$C_{19}H_{20}Br_2N_2O_3$	125	5.79	5.91	33.06	33.19
3	C_4H_8NO	Br	$C_{16}H_{20}Br_2N_2O_4$	99 *213	6.03	6.09	34.48	34.10
4	$C_5H_{10}N$	Br	$C_{17}H_{22}Br_2N_2O_3$	101 *178	6.06	6.21	34.63	34.73
5	2-Cl.C_6H_4NH	Br	$C_{18}H_{17}Br_2ClN_2O_3$	193	5.55	5.72	32.21	31.97
6	2-CH_3.C_6H_4NH	Br	$C_{19}H_{20}Br_2N_2O_3$	157	5.79	5.68	33.06	33.23
7	4-CH_3.C_6H_4NH	Br	$C_{19}H_{20}Br_2N_2O_3$	116	5.79	5.82	33.06	33.21
8	2-OCH_3.C_6H_4NH	Br	$C_{19}H_{20}Br_2N_2O_4$	165(d)	5.60	5.91	31.99	32.09
9	2-OC_2H_5.C_6H_4NH	Br	$C_{20}H_{22}Br_2N_2O_4$	162(d)	5.45	5.64	31.13	32.82
10	3-HO.C_6H_4NH	Br	$C_{18}H_{18}Br_2N_2O_4$	120	5.76	5.87	32.93	33.28
11	n-C_4H_9NH	I	$C_{16}H_{22}I_2N_2O_3$	107	5.15	5.40	46.69	47.00
12	C_4H_8NO	I	$C_{16}H_{20}I_2N_2O_4$	220	5.02	5.24	45.52	45.91
13	$C_5H_{10}N$	I	$C_{17}H_{22}I_2N_2O_3$	135	5.04	4.99	45.67	45.54
14	$(C_2H_5)_2N$	I	$C_{16}H_{22}I_2N_2O_3$	... *179	5.15	5.31	46.60	46.82
15	$(C_6H_{11})_2N$	I	$C_{24}H_{34}I_2N_2O_3$	... *183(d)	7.49	7.63	40.43	40.25
16	$C_6H_{11}NH$	I	$C_{18}H_{24}I_2N_2O_3$	... *199(d)	4.91	5.06	44.55	44.65
17	C_6H_5NH	I	$C_{18}H_{18}I_2N_2O_3$	180	4.96	5.11	45.03	45.16
18	2-CH_3.C_6H_4NH	I	$C_{19}H_{20}I_2N_2O_3$	187	5.69	5.82	43.94	44.08

* Hydrochlorides.

TABLE—2

LOCAL ANESTHETIC ACTIVITY OF



(A) *Surface anesthesia*

Sl. No.	R	Drug conc. in %age (approx.)	%age anesthesia	Duration in minutes	Potency compared to cocaine	Potency compared to lignocaine
1.	morpholino	0.2	90.00	15.00	½	equal
2.	piperidino	0.4	100.00	22.00	½	½
3.	n-butylamino	0.2	90.00	15.50	½	equal
4.	cocaine	0.1	96.66	21.00	...	...
	lignocaine	0.2	100.00	14.83	...	...

(B) *Intradermal Anesthesia*

Sl. No.	R	Drug conc. in % age (approx.)	% age anesthesia	Duration in minutes	Potency compared procaine	Potency compared to lignocaine
1.	morpholino	0.4	97.00	65.00	equal	½
2.	piperidino	0.4	98.00	75.00	equal	½
3.	n-butylamino	0.4	95.00	72.00	equal	½
	procaine	0.4	100.00	55.83	...	½
	lignocaine	0.2	98.33	44.86	...	...

Found : N, 3.99% ; Br, 48.08% ;
$C_{10}H_{11}Br_2NO_3$ required : N, 4.16% ; Br, 48.05%.

Preparation of 3, 5-diiodo propesin :

Propesin (0.1 *M*) was dissolved in aq. HCl (50%, 300 ml) and iodine monochloride in aq. HCl 12.5%, 300 ml) was added with stirring until no more precipitates were obtained. The contents were diluted with excess of water and stirring was continued for some time. The product separated as light brown precipitates which was crystallised form ethanol, m. p. 113°.

Found : N, 3.30% ; I, 58.82%
$C_{10}H_{11}I_2NO_3$ required : N, 3.25% ; I, 58.92%;

Chloroacetylation of dihalo propesin :

3,5-Dibromo/diiodo propesin (0.05*M*) in dry, thiophene free benzene (50 ml) and chloroacetyl chloride (0.12*M*) in dry, thiophene free benzene (50 ml) were refluxed on a water-bath for 3-4 hours. Benzene was distilled off to obtain the product which was washed with aq. $NaHCO_3$ (4%) and water, filtered, dried and crystallised from ethanol.

N-Chloroacetyl-3,5-dibromo propesin, m.p. 182°.
Found : N 3.51% ; Br, 39 00% ;
$C_{12}H_{12}ClBr_2NO_3$ required : N 3.38% ; Br, 38.78%.

N-Chloroacetyl-3,5-diiodo propesin, m.p. 186°.
Fonnd : N, 2.89% ; I, 50.10% ;
$C_{12}H_{12}ClI_2NO_3$ required : N, 2.75% ; I, 49.99%.

Preparation of N-substituted-3,5-dibromo/diiodo propesin derivatives :

N-Chloroacetyl-3,5-dibromo/diiodo propesin (0.05*M*) in absolute ethanol (15 ml) and the amine (0.12*M*) in absolute ethanol (15 ml) were refluxed on a water-bath for 7-9 hrs. The contents were cooled and poured on to ice-water. The product was filtered, washed with dil. HCl (4%) and water, crystallised from ethanol.

The physical and analytical data of these compounds are listed in Table 1.

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Synthesis of Some New 1, 3, 4-Oxa(thia)diazoles and 1,2,4-Triazoles as Potential Fungicides

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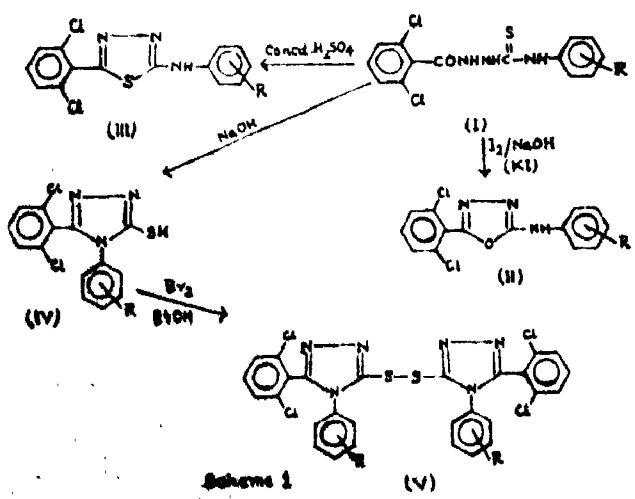
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Several 2-arylamino-5-(2, 6-dichlorophenyl)-1, 3, 4-oxadiazoles (II), the corresponding thiadiazoles (III) and 4-aryl-5-(2, 6-dichlorophenyl)-3-mercapto-1, 2, 4-triazoles (IV) have been prepared by the cyclisation of corresponding 4-aryl-1-(2, 6-dichlorobenzoyl) thiosemicarbazides (I). Oxidation of the triazoles (IV) has furnished the corresponding bis-triazolyl disulphides (V). Four of the tested compounds have shown the fungitoxicity against Aspergillus niger and Aspergillus flavus comparable to that of the Dithane M-45, a commercial fungicide at 1000 ppm and 100 ppm.

MANY agricultural fungicides contain reactive chlorine atoms, and 1,3,4-oxadiazole[1-3], 1,3,4-thiadiazole[4,5] and 1,2,4-triazole[6-9] derivatives also possess various useful biological activities. It was, therefore, speculated that the insertion of 2,6-dichlorophenyl moiety into the biologically versatile heterocycles might result in the fungicides of better performance.

The 1,3,4-oxadiazoles(II), corresponding thiadiazoles(III), 1,2,4-triazoles(IV) and the bis-triazolyl disulphides(V) have been prepared according to the Scheme 1. The required 4-aryl-1-(2,6-dichlorobenzoyl) thiosemicarbazides(I) were prepared by treating 2,6-dichlorobenzoylhydrazine with aryl *iso*-thiocyanates in ethanol[10]. The compounds were characterised by their elemental analyses and ir spectra.



Scheme 1

Sixteen of the title compounds have been screened for their antifungal activity against *A. niger* and *A. flavus*. The results obtained have been compared with *Dithane M-45*, a commercial fungicide, which was also tested under similar conditions. Four of these compounds exhibited the antifungal activity almost in the range of the commercial fungicide at concentrations 1000 ppm and 100 ppm. However, the bis-triazolyl disulphides(V) were found to be more active than the corresponding oxadiazoles(II), thiadiazoles(III) and triazoles(IV).

Experimental

The ir spectra (in KBr) were recorded on a Perkin-Elmer, model 521, spectrophotometer.

2,6-Dichlorobenzoylhydrazine was prepared by the method of Covello *et al*[11].

4-Aryl-1-(2,6-dichlorobenzoyl)thiosemicarbozides (I) were prepared according to the method of Silberg and Cosma[10]. The I thus prepared are as follows: R=H, m.p. 183° (Found: N, 12.06; S, 9.39, $C_{14}H_{11}Cl_2N_3OS$ requires N, 12.35; S, 9.41%); R=*p*-Cl, m.p. 166° (Found: N, 11.12; S, 8.21, $C_{14}H_{10}Cl_3N_3OS$ requires N, 11.21; S, 8.54%); R=*p*-OCH_3, m.p. 179° (Found: N, 11.07; S, 8.73, $C_{15}H_{13}Cl_2N_3O_2S$ requires N, 11.35; S, 8.65%); R=*m*-CH_3, m.p. 196° (Found: N, 12.03; S, 8.84, $C_{15}H_{13}Cl_2N_3OS$ requires N, 11.86; S, 9.04%) and R=*p*-CH_3, m.p. 184° (Found: N, 11.55; S, 9.21, $C_{15}H_{13}Cl_2N_3OS$ requires N, 11.86, S, 9.04%). These compounds were recrystallised from ethanol, and their yield ranged from 78-90%.

2-Arylamino-5-(2,6-dichlorophenyl)-1,3,4-oxadiazoles(II) were prepared following the method of

* For correspondence

Silberg and Cosma[10], and were recrystallised from ethanol. The oxadiazoles(II) thus prepared are recorded in Table 1A.

2-Arylamino-5-(2, 6-dichlorophenyl)-1, 3, 4-thiadiazoles(III)— These were prepared according to the method of Maffii *et al*[13], and were recrystallised from ethanol. The thiadiazoles(III) thus prepared are recorded in Table 1B.

4-Aryl-5-(2, 6-dichlorophenyl)-3-mercapto-1, 2, 4-triazoles(IV) were prepared[12] from the thiosemicarbazides (I), and were recrystallised from ethanol. The triazoles(IV) thus prepared are recorded in Table 1C.

Bis[4-aryl-5-(2,6-dichlorophenyl)-1,2,4-triazol-3-yl] disulphides(V) were prepared by the oxidation of 3-mercapto-1,2,4-triazoles(IV) with bromine. Thus an ethanolic solution of the compound IV (0.02*M*) was stirred with bromine (0.02*M*) in ethanol (15 ml.). The disulphide compound at once began to separate, it was filtered, and recrystallised from ethanol. The bis-triazolyl disulphides(V) thus prepared are recorded in Table 1C.

Fungicidal Screening

The antifungal activity was evaluated by agar-plate technique[14] against *A. niger* and *A. flavus* at concentrations 1000 ppm, 100 ppm and 10 ppm.

Table 1A—2-Arylamino-5-(2, 6-dichlorophenyl)-1, 3, 4-oxadiazoles(II)

Sl. No.	R	Yield %	m.p. °C	Mol. formula	C(%) Found	C(%) Calcd	H(%) Found	H(%) Calcd
1[a]	H	78	209	$C_{14}H_9Cl_2N_3O$	54.72	54.90	2.80	2.94
2	*p*-Chloro	80	216	$C_{14}H_8Cl_3N_3O$	48.18	48.44	2.09	2.35
3[b]	*p*-Methoxy	75	231	$C_{15}H_{11}Cl_2N_3O_2$	53.29	53.57	3.14	3.27
4	*m*-Methyl	72	225	$C_{15}H_{11}Cl_2N_3O$	56.06	56.25	3.16	3.44
5	*p*-Methyl	76	236	$C_{15}H_{11}Cl_2N_3O$	56.38	56.25	3.28	3.44

Significant bands (cm^{-1}) in ir spectra (in KBr)

	C=N,	C—O—C,	N—H,	Substituted benzene nucleus
a.	1635	1024	3420	1600, 1585, 780, 745
b.	1630	1020	3455	1600, 1580, 850, 800

Table 1B—2-Arylamino-5-(2, 6-dichlorophenyl)-1, 3, 4-thiadiazoles(III)

Sl. No.	R	Yield %	m.p. °C	Mol. formula	N% Found	N% Calcd.	S% Found	S% Calcd.
6	H	70	283	$C_{14}H_9Cl_2N_3S$	12.87	13.04	9.79	9.94
7[a]	*p*-Chloro	75	225	$C_{14}H_8Cl_3N_3S$	11.89	11.78	8.91	8.98
8	*p*-Methoxy	72	209	$C_{15}H_{11}Cl_2N_3OS$	11.81	11.93	8.87	9.09
9[b]	*m*-Methyl	68	185	$C_{15}H_{11}Cl_2N_3S$	12.19	12.50	9.36	9.52
10	*p*-Methyl	75	193	$C_{15}H_{11}Cl_2N_3S$	12.61	12.50	9.62	9.52

Significant bands (cm^{-1}) in ir spectra (in KBr)

	C=N,	C—S—C,	N—H,	Substituted benzene nucleus
a.	1625	715	3380	1595, 1575, 850, 775
b.	1632	710	3410	1602, 1580, 800, 780

Table 1C—4-Aryl-5-(2, 6-dichlorophenyl)-3-mercapto-1, 2, 4-triazoles (IV) and their disulphides(V)

Sl. No.	R	Yield %	m.p. °C	Mol. formula	N(%) Found	N(%) Calcd.	S(%) Found	S(%) Calcd.
				4-Aryl-5-(2,6-dichlorophenyl-3-mercapto-1,2,4-triazoles(IV)				
11	H	82	208	$C_{14}H_9Cl_2N_3S$	12.91	13.04	9.75	9.94
12[a]	*p*-Chloro	84	233	$C_{14}H_8Cl_3N_3S$	11.53	11.78	8.84	8.98
13	*p*-Methoxy	80	241	$C_{15}H_{11}Cl_2N_3OS$	11.89	11.93	8.86	9.09
14	*m*-Methyl	78	239	$C_{15}H_{11}Cl_2N_3S$	12.67	12.50	9.70	9.52
15[b]	*p*-Methyl	85	246	$C_{15}H_{11}Cl_2N_3S$	12.36	12.50	9.39	9.52
				bis[4-Aryl-5-(2, 6-dichlorophenyl)-1, 2, 4-triazol-3-yl] disulphides(V)				
16[c]	H	68	181	$C_{28}H_{16}Cl_4N_6S_2$	13.16	13.08	9.83	9.97
17	*p*-Chloro	70	204	$C_{28}H_{14}Cl_6N_6S_2$	11.59	11.81	8.85	9.00
18	*p*-Methoxy	65	198	$C_{30}H_{20}Cl_4N_6O_2S_2$	11.78	11.97	8.06	9.12
19[d]	*m*-Methyl	62	200	$C_{30}H_{20}Cl_4N_6S_2$	12.74	12.54	9.41	9.55
20	*p*-Methyl	66	207	$C_{30}H_{20}Cl_4N_6S_2$	12.42	12.54	9.36	9.55

Significant bands (cm^{-1}) in ir spectra (in KBr)

	C=N,	S—H,	Substituted benzene nucleus
a.	1615	2580	1600, 1580, 845, 780
b.	1620	2600	1602, 1585, 800, 775
c.	1622	—	1600, 1580, 790, 760
d.	1630	—	1600, 1578, 815, 765

The number of replications in each case was three. The percentage inhibitions by various compounds are recorded in Table 2.

$$\% \text{ Inhibition} = \frac{(C-T)\times 100}{C}$$

where, C = Diameter of fungus colony in control plates after 96 hours.
T = Diameter of fungus colony in treated plates after 96 hours.

Results and Discussion

All the tested compounds exhibited significant fungitoxicity at 1000 ppm but their toxicity decreased markedly on dilution except in case of the compound No. 17-20 which are the representatives of bis-triazolyl disulphides(V), and inhibited the growth of both the fungal species>50% even at 10 ppm. The fungitoxicity of the compounds varied with fungal species as well, but no generalisation could be made in this regard (Table 2).

TABLE 2—FUNGICIDAL SCREENING

Compound serial as in Tables 1A, 1B & 1C	AVERAGE PERCENTAGE INHIBITION AFTER 96 HOURS					
	Organism—*A. niger* Concentrations used			Organism—*A. flavus* Concentrations used		
	1000 ppm	100 ppm	10 ppm	1000 ppm	100 ppm	10 ppm
2	87.1	61.6	32.4	91.8	55.1	25.8
3	100	62.7	31.8	95.0	52.8	30.1
4	82.9	59.4	32.3	86.8	50.3	21.8
5	86.3	60.5	31.7	92.5	49.2	23.2
7	85.4	60.4	30.6	89.6	53.2	25.1
8	100	61.3	29.7	92.3	52.1	28.3
9	82.6	58.2	29.8	86.4	49.6	19.2
10	85.7	58.9	29.6	90.2	49.9	21.7
12	90.2	68.8	40.4	83.6	63.2	47.4
13	85.4	62.1	41.2	91.1	53.4	41.2
14	82.8	64.5	39.3	80.4	62.8	39.5
15	88.7	59.3	43.0	88.5	54.7	38.4
17	100	84.6	53.7	98.5	78.8	51.3
18	98.8	85.0	54.1	100	79.2	50.4
19	100	83.9	50.6	96.4	80.8	51.5
20	100	83.8	52.4	99.3	79.0	52.7
Dithane M-45 (A commercial fungicide)	100	85.2	72.4	95.7	81.2	66.2

These results show that the oxadiazoles (II, Compound Nos. 2-5) were relatively more fungitoxic than their thiadiazole analogues (III, Compound Nos. 7-10) but the difference in their fungicidal action was of very low order. In general, the bis-triazolyl disulphides (V, Compound Nos. 17-20) were more potent than the parent triazoles (IV, Compound Nos. 12-15), and the level of their fungitoxicity was also very high. This could be expected from their structures (Fig. 1) which have condition for S—S bond fission apparently analogous to that of thiram (Fig. 2), a common fungicide, where it has been suggested[15] that it reacts with thiols, the important cellular constituents, and the mechanism of the reaction involves S—S bond fission.

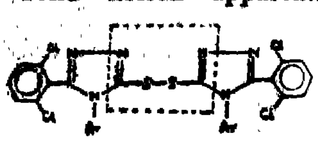


Fig. 1

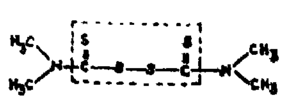


Fig. 2

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Search for Potent Anti-viral Agents : Synthesis of 2-Phenyl-3-Benzimidazolyl-alkyl/arylalkyl 6-Bromo-Quinazolin (3H)-4-ones as Possible Anti-viral Agents

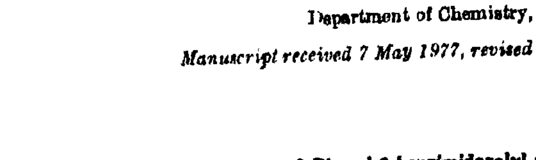
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Fifteen new 2-Phenyl-3-benzimidazolyl-alkyl/arylalkyl-6-bromo-quinazolin (3H)-4-ones were prepared and tested for antiviral activity against Vaccinia and Ranikhet viruses, but contrary to our expectations none of them was found to possess significant activity.

BENZIMIDAZOLES have been reported to be very active against different viruses[1-3]. Quinazolones have been found to show diverse pharmacological activities mainly as C.N.S. depressants[4-6] and recently have been reported as anti-virals[7]. As the presence of both the nuclei viz. Quinazolone and benzimidazole in a single compound might result in a potent anti-viral compound, we have synthesised 2-phenyl-3-benzimidazolyl-alkyl / arylalkyl-6-bromo-quinazoliu(3H)-4-ones of type (I) by the condensation of 2-phenyl-3-carboxyalkyl/aryl-6-bromo-quinazolin (3H)-4-ones with substituted *o*-phenylene diamines and tested then for anti-viral activity.



where X = (i) $-CH_2-$ (ii) $-CH_2-CH_2-$, (iii) $-CH(CH(Me)_2)-$, (vi) $-CH(CH_2-CH(Me)_2)-$, (v) $-CH(CH_2-C_6H_5)-$

(a) Y = H, Z = H
(b) $Y = CH_3$, $Z = CH_3$
(c) Y = Cl, Z = H

Experimental

All the melting points are taken in open capillaries and are uncorrected.

(i) 5-Bromo-anthranilic acid : This was prepared by the method of Wheeler and Oats[8], m.p. (210-212°).

(ii) 6-Oxo-2-phenyl-4,5-(3'-bromobenzo)-1,3-oxazin : This was prepared by the method of Sammour, Fahmy and Mahmoud[9] m.p. (204-205°).

(iii) 6-Bromo-2-phenyl-3-carboxyalkyl/arylalkyl quinazolin (3H)-4-ones : These were prepared by the method of Misra et al.[10].

(iv) 2-Phenyl-3-benzimidazolyl-alkyl/arylalkyl-6-bromo-quinazolin (3H)-4-ones :

These compounds were prepared by adopting the method of Pool, Harwood and Ralston[11]. An equimolar (0.05 mole) mixture of 6-bromo-2-phenyl-3-carboxyalkyl/arylalkyl-quinazolin(3H)-4-ones and simple or substituted *o*-phenylenediamine was heated at its boiling point for 30 minutes in an oil bath. The products were isolated and recrystallized from dilute ethanol. The physical constants of the compounds are recorded in Table I.

Anti viral Screening : All the 15 compounds were tested for anti-viral activity against Ranikhet and Vaccinia viruses in a stationary culture of Chorio-allantoic membrane of chick embryo at a drug dilution of 0.05 mg/ml by HA test[12]. The compounds used against the Ranikhet and Vaccinia Viruses were 0.064 HA/ml and 50 PFU/ml respectively. Contrary to our expectations none of the compounds showed significant anti-viral activity.

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TABLE—1

PHYSICAL CONSTANTS OF 2-PHENYL-3-BENZIMIDAZOLYL ALKYL/ARALKYL 6-BROMO QUINAZOLIN (3H)-4-ONES OF TYPE I.

Sl. No.	X	Y	E	M.P.°C	% Yield	Mol formular	% N Found	% N Calc.
*1.	$—CH_2—$	H	H	155	55	$C_{22}H_{15}N_4OBr$	13.24	13.31
2.	$—CH_2—$	CH_3	CH_3	165	75	$C_{24}H_{19}N_4OBr$	12.70	12.20
3.	$—CH_2—$	Cl	H	175	60	$C_{22}H_{14}N_4OClBr$	12.50	12.03
4.	$—CH_2\text{-}CH_2—$	H	H	170	50	$C_{23}H_{17}N_4OBr$	12.60	12.58
*5.	$—CH_2\text{-}CH_2$	CH_3	CH_3	190	80	$C_{25}H_{21}N_4OBr$	11.98	11.83
6.	$—CH_2\text{-}CH_2$	Cl	H	260	75	$C_{23}H_{16}N_4OClBr$	12.56	12.07
7.	$CH\text{-}(CH_3)_2$ / —CH—	H	H	180	65	$C_{25}H_{21}N_4OBr$	13.32	11.83
8.	$CH\text{-}(CH_3)_2$ / —CH—	CH_3	CH_3	165	58	$C_{27}H_{25}N_4OBr$	11.66	11.17
9.	$CH\text{-}(CH_3)_2$ / —CH—	Cl	H	156	60	$C_{25}H_{20}N_4OClBr$	11.60	11.30
10.	$CH_2\text{-}CH(CH_3)_2$ / —CH—	H	H	230	70	$C_{26}H_{23}N_4OBr$	11.54	11.48
11.	$CH_2\text{-}CH(CH_3)_2$ / —CH—	CH_3	CH_3	210	72	$C_{28}H_{27}N_4OBr$	10.64	10.87
12.	$CH_2\text{-}CH(CH_3)_2$ / —CH—	Cl	H	190	80	$C_{26}H_{22}N_4OClBr$	11.22	10.73
13.	$CH_2C_6H_5$ / —CH—	H	H	160	78	$C_{29}H_{21}N_4OBr$	11.24	10.76
*14.	$CH_2C_6H_5$ / —CH—	CH_3	CH_3	195	60	$C_{31}H_{25}N_4OBr$	9.70	10.20
15.	$CH_2C_6H_5$ / —CH—	Cl	H	180	55	$C_{29}H_{24}N_4OClBr$	10.60	10.08

		Found	Calc.
*(1)	%C	59.00	59.47
	%H	3.32	3.65
(5)	%C	63.42	63.58
	%H	4.00	4.44
(14)	%C	58.78	58.81
	%H	4.40	4.55

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A Comparative Study of Glucose-6-phosphate Dehydrogenase in Ehrlich Ascites Carcinoma and Host's Liver

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Glucose-6-phosphate dehydrogenase was studied in Ehrlich ascites carcinoma and compared with that of the host's liver. Distinct differences were observed in thermal stability, *p*H optima and Km for Glucose-6-phosphate. However, no difference in the electrophoretic mobilities on polyacrylamide gel was observed.

GLUCOSE-6-phosphate dehydrogenase (G-6-PD) attracted the attention of several workers in the field of cancer-research[1,2,3]. It was reported to be increased in variety of experimentally induced and spontaneous tumours[4,5,6]. Recently, it has been observed in our laboratory that liver G-6-PD increases proportionally with the growth of Ehrlich ascites carcinoma (EAC) and induced skin carcinoma[7]. It was, therefore, decided to compare the behaviour of this enzyme in Ehrlich ascites carcinoma with that of the host's liver.

Experimental

EAC was maintained in Swiss male mice by intraperitoneal inoculation of ascitic fluid.

Ascites cells were taken out from the peritoneal cavity and washed thrice in cold 0.1*M* Na-K-phosphate buffer. *p*H 7.2 containing 5 mM $MgCl_2$ and finally resuspended in such a way, so that the suspension contains 4 mg dry wt/ml in this buffer. While vigorously agitated on a Vortex mixer, 0.01 vol of toluene : ethanol (1 : 9 v/v) was added to the cell-suspension and the agitation continued for a further period of 10 mins. The toluene treated cells[8] was then kept in ice.

10% liver homogenate from normal and tumour-bearing mice was prepared in cold 0.25*M* sucrose. Both the toluene-treated ascites cell-suspension and the liver homogenates were centrifuged at 100,000 g for 1 hr and the supernatants were used for enzyme assay. G-6-PD was assayed spectrophotometrically[9] by following optical density change at 340 nm. Specific activity was expressed as micromoles of NADPH produced/milligram of protein/minute.

Michaelis constant of G-6-P at 0.15 mM NADP concentration was determined at *p*H 7.5, using concentration of G-6-P ranging from 0.1 to 1.5 mM for liver enzyme and from 0.01 to 0.5 mM for tumour enzyme. The Km values of NADP at 1.0 mM and 0.1 mM concentration of G-6-P for liver and tumour enzymes respectively, were also determined at *p*H 7.5 with concentrations of NADP ranging from 0.015 to 0.21 mM.

Electrophoresis of G-6-PD of samples was carried out with soluble supernatant on 5.5% polyacrylamide gel at *p*H 7.5 and stained according to the method of Dietz *et al.*[10].

Results

pH optima : G-6-PD activities of ascites cells as well as host's liver at different *p*H are shown in Fig 1. Enzyme preparation from normal and host's liver shows peak at *p*H 8, whereas, the *p*H optima of ascites cell preparation is *p*H 7.5. It is also evident from the figure that the specific activity of the enzyme is much higher in tumour cells than that of the host's liver.

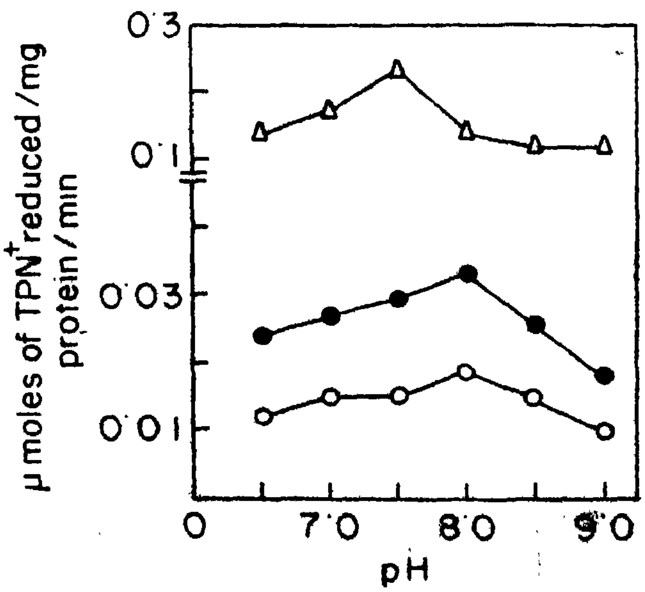


Fig. 1. Specific activity of G-6-PD with respect to *p*H, normal liver (O—O) ; host's liver (●—●) ; EAC (▲—▲)

Thermal stability : Heat inactivation studies of enzyme preparations were carried out at 45° and 55° according to Messina *et al*[12]. Enzymes in all preparations were inactivated at 55°. Whereas, it can be observed from Fig 2 that at 45°, the host's liver enzyme retains about 60% of the initial activity at the end of 10 minutes. The tumour cell enzyme seems to be more heat-labile which is evident from the figure.

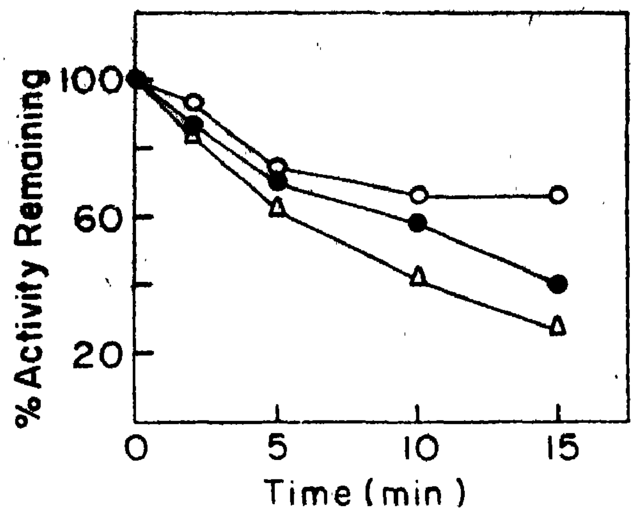


Fig. 2. Thermal stability studies of G-6-PD, normal liver (O—O) ; host's liver (●—●) ; EAC (Δ—Δ).

Electrophoretic mobility :

Enzyme preparation from both tumour cells and host's liver demonstrated one band on activity staining with same mobility on 5.5% polyacrylamide gel at *p*H 8.3. The band is more distinct in host's liver preparation in comparison to that of the toluene-treated ascites cells.

Discussions

It is well known that the tumour tissues have a high rate of aerobic glycolysis. Hexose monophosphate shunt being an oxidative pathway is also higher in tumours. The activity of G-6-PD, the first enzyme of the shunt pathway, has been found to be increased in tumour cells[4,5] and also in host's liver[7]. From the results presented in this communication it shows that the specific activity of G-6-PD is much higher in toluene-treated ascites cells in comparison to that of the host's liver. It may also be mentioned here that the enzyme from EAC although has a much higher affinity for G-6-P than the liver enzymes, it is very much susceptible to G-6-P. This enzyme is significantly inhibited by G-6-P at a concentration higher than 0.6 mM whereas the liver enzymes (both normal and host's) are not inhibited even at a concentration of 1.5 mM (data not shown). This means that the EAC enzyme shows substrate inhibition at high concentration whereas the liver enzymes are not. An attempt to compare the behaviour of the enzyme in liver and ascites cells reveals a marked difference in thermal stability and *p*H optima. It can thus be concluded that host's liver G-6-PD, the activity of which increases with the growth of the ascites tumour, behaves like the normal liver enzyme and thus differs significantly from the G-6-PD of toluene-treated ascites cells.

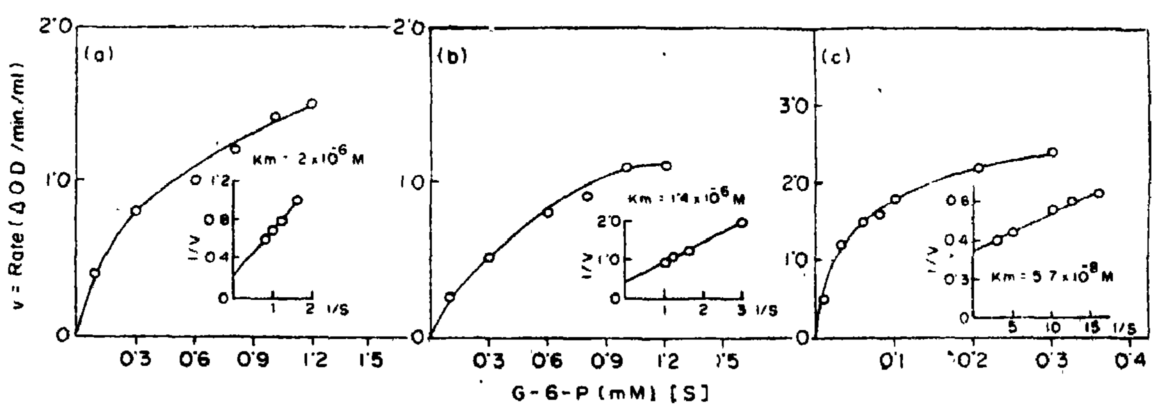


Fig. 3. Substrate concentration curves of G-6-PD,
(a) Normal liver,
(b) host's liver,
(c) Ehrlich ascites cells.
Insets represent double reciprocal plot from where Kms were calculated.

Michaelis-Menten constants : In case of host's liver, the Km for G-6-P ($1.4 \times 10^{-6} M$) is similar in magnitude with that of normal liver (Fig 3), whereas in ascites cells, the Km is significantly lower and is $5.7 \times 10^{-8} M$ (Fig 3). There is not much of difference in Km values for NADP in host's liver and ascites cell ($7.7 \times 10^{-7} M$ and $1.1 \times 10^{-7} M$ respectively) enzymes. In normal liver, the Km value for NADP has been found to be $1 \times 10^{-6} M$.

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Titrimetric Determination of Iron(III), Molybdenum(VI) and Vanadium(V) after Reduction with Aluminium Amalgam[@]

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Use of aluminium amalgam as a reducing agent is investigated with a view to its applications to the estimation of iron(III), molybdenum(VI) and vanadium(V). The pieces of aluminium metal are lightly coated with mercury by treatment with mercuric chloride solution and are used in dil. HCl or dil. H_2SO_4 for iron(III), molybdenum(VI) and vanadium(V). *The process requires 10 to 15 minutes and the reduction to the lower state is quantitative.* The aluminium metal is cheaper than either zinc or silver. *This procedure is simple and can be profitably adopted for routine estimations.* Interference caused by some commonly associated ions is investigated.

SEVERAL metals can be estimated by reducing them to lower oxidation states by using zinc metal in a Jones reductor. The rates of reduction of iron(III), molybdenum(VI), vanadium(V), titanium(IV), chromium(III), niobium(V) were increased by using zinc amalgam instead of zinc[1]. It was found that by the time 2 per cent. of the zinc has been consumed the reduction becomes too slow to be of any practical value[2]. Riegel and Schwartz also found that the zinc amalgam method was inconvenient. They suggested the use of aluminium powder to reduce iron[3] and molybdenum[4]. However aluminium powder is inconvenient as it needs special preparation. Methods in which various other forms of pure aluminium metal such as aluminium foils are used for reduction of iron have also been investigated[5]. Estimation of ferric iron by silver reductor was studied by Walden, Hammet and Edmond[5] ; Henry and Gelbach[6]. Birnbaum and Walden[7] used the silver reductor for the molybdenum(VI). Although silver has high reducing power in high acidic medium, it is commercially unsuitable. An attempt has been made to reduce vanadium(V) to vanadium(III) by mercury reductor in hydrochloric acid medium[8], however it is incapable of reducing vanadium(V) to vanadium(III) in sulphuric acid medium. This reductor doesn't reduce vanadium(V) to vanadium(II).

In the present work the authors found that aluminium amalgam is more suitable than any other previously reported reducing agent for iron, molybdenum and vanadium.

Experimental

Materials

All chemicals used were A.R. grade and glass distilled water was used throughout.

0.01 N Potassium Permanganate

Dissolve 0·158 g of potassium permanganate to give 500 ml solution and standardize with ferrous ammonium sulphate[9].

Iron(III) Solution

Dissolve 10.760 g of ferric ammonium sulphate crystals to give 100 ml solution. And 5 ml dilute sulphuric acid before dilution. An aliquot is reduced with $SnCl_2$ and the resulting ferrous iron is estimated with permanganate[9].

Molybdenum(VI) Solution

Dissolve 2.300 g of ammonium molybdate in water to give 100 ml solution and standardize by iodometric reduction method[10].

Vanadium(V) Solution

Dissolve 2.868 g of ammonium meta-vanadate in water to give 100 ml solution and standardize by potassium iodate method[9].

Amalgamated Aluminium

Treat 5 mm × 5 mm pieces of 1 mm thick sheet of iron-free aluminium with 5% solution of mercuric chloride for 5-10 minutes and wash thoroughly with distilled water. The same solution of $HgCl_2$ can be repeatedly used several times.

Apparatus

Jones reductor is a 12 cm diameter, 22 cm long column with a stopcock at one end.

Procedure

(a) Reduction of iron(III) to iron(II) :

Transfer an aliquot of solution containing about 8-10 mg of iron to the reductor column, acidifing

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@ Presented to the Annual Convention of Chemist Roorkee, 1975.

the solution with 5N sulphuric acid or 5N hydrochloric acid to give the acidity 0.5N and 0.25N respectively in the final volume of 25 ml. Wait for 10-15 minutes and then titrate the reduced iron(II) solution against 0.01 N potassium permanganate.

(b) Reduction of molybdenum(VI) to molybdenum(III) :

Transfer an aliquot of the solution containing 8-10 mg of molybdenum(VI) as ammonium molybdate solution to the reductor column, acidifing with exact quantity of 5N sulphuric acid or 5N hydrochloric acid to give acidity 0.5N and 0.25N respectively in the final volume of 25 ml. Wait for 10-15 minutes and then collect the reduced solution along with water washings in a conical flask containing excess of acidified ferric alum and 5 ml of syrupy phosphoric acid[9] to avoid air oxidation of molybdenum(III). Titrate the contents against 0.01N potassium permanganate.

(c) Reduction of vanadium(V) to vanadium(II)

Transfer an aliquot of the solution containing 8-10 mg of vanadium(V) as ammonium meta-vanadate solution to the reductor column, acidifing with exact quantity of 5N sulphuric acid or 5N hydrochloric acid to give acidity 0.5N and 0.25N respectively in the final volume of 25 ml. Wait for 10-15 minutes to complete the reduction. The progress of the reduction can be seen from the colour changes (viz. yellow-blue-green-violet). Vanadium(V) forms VO_2^+ ions of yellow colour in acid medium. On reduction the vanadium(IV) ion is first produced in the form of aquovanadyl $[VO(H_2O)_5]^{2+}$ of blue colour. Further the vanadium(III) is produced in the form of aquo ions $[V(H_2O)_6]^{3+}$ of green colour. Finally the vanadium(II) ion is produced in the form of aquo ions $[V(H_2O)_6[^{2+}$ of violet colour. If the ions $[V(H_2O)_6]^{3+}$ and $VO(H_2O)_5^{2+}$ are simultaneously present in the solution, an intermediate compound of brown colour, that has the bridged group $[VOV]^{4+}$ is formed and there is brownis heing which latter on changes to violet. Collect the reduced solution along with water washings in a conical flask containing excess of acidified ferric solution and 5 ml of syrupy phosphoric acid to avoid air oxidation of vanadium[11](II). Titrate the contents against 0.01N potassium permanganate.

Results and Discussion

It is observed that reduction with aluminium amalgam is possible only in acidic medium, particularly between the acidity range of 0.5 to 2.5N for sulphuric acid and 0.25 to 2.0N for hydrochloric acid. Above this concentration reaction is vigorous and difficult to control. Sometimes the contents of the column are spirted out.

The rate of reduction directly corresponds to the acidity of the solution particularly in hydrochloric acid solution. In hydrochloric acid medium the potential of Hg_2Cl_2/Hg couple decreases, so the efficiency of the reductor increases. Quantitative reduction of iron(III), molybdenum(VI) and vanadium(V) to iron(II), molybdenum(III) and vanadium(II) is possible by this reductor even at low acidity due to great difference in the standard redox potential of the reductant and oxidant systems.

The quantitative nature of the vanadium(V) reduction is confirmed by comparing the absorption spectra of vanadium(III) produced from mercury reductor in hydrochloric acid medium[8] and vanadium(III) produced by this method. Both of these have absorption maxima at 420 nm and 600 nm. Identical nature of the spectra shows quantitative reduction of vanadium(V) to vanadium(III) state by aluminium amalgam. Spectral characteristics of vanadium(IV) obtained by oxidation of vanadium(III) is in agreement with the spectral characteristics of vanadium(IV) obtained by mercury reductor in sulphuric acid medium[8] (Fig. 1).

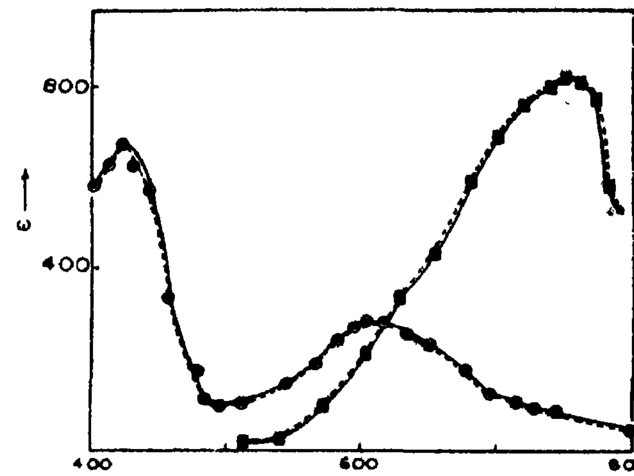


Fig. 1 : Absorption spectra of 0.021M solution of Vanadium(III) and Vanadium(IV)

Vanadium (III) : -○- = Mercury reductor method ;
-●- = Aluminium amalgam method.

Vanadium (IV) : -□- = Mercury reductor method ;
-■- = Aluminium amalgam method.

The present method for the determination of vanadium is more convenient when compared with earlier reported methods.

Reactivity of aluminium amalgam increases with time and evolution of hydrogen becomes rapid[12]. The reaction with water is exothermic, heat liberated keeps the solution hot and it speeds up the reaction. Results obtained are given in Tables 1, 2 and 3.

Silver reductor process is commercially unsuitable due to the high cost of silver metal, though the reduction can be carried out at the HCl molarity range of 0.5 to 1.5. Aluminium powder procedure for iron and molybdenum is inconvenient as it requires special preparation of powder and heating of the solution is also essential along with high

TABLE—1 REDUCTION OF Fe(III) TO Fe(II) AND FURTHER PERMANGANOMETRIC DETERMINATION

Iron(III) taken mg	Iron(II) found mg	Standard deviation of 5 observations
10.05	10.05	±0.010
19.50	19.51	±0.011
45.00	44.96	±0.013
62.20	62.16	±0.020

TABLE—2 REDUCTION OF Mo(VI) TO Mo(III) AND FURTHER PERMANGANOMETRIC DETERMINATION

Molybdenum(VI) taken mg	Molybdenum(III) found mg	Standard deviation of 5 observations
9.53	9.508	±0.028
25.00	25.05	±0.017
42.20	42.25	±0.019
50.00	49.96	±0.015

TABLE—3 REDUCTION OF V(V) TO V(II), SUBSEQUENT REDUCTION OF Fe(III) TO Fe(II) AND PERMANGANOMETRIC DETERMINATION

Vanadium(V) taken mg	Vanadium(II) found mg	Standard deviation of 5 observations
7.22	7.20	±0.030
28.56	28.60	±0.021
50.25	50.30	±0.018
60.10	60.07	±0.015

acidity ranges. Mercury reductor is also incapable of reducing vanadium(V) to vanadium(III) in either sulphuric or hydrochloric acid medium[8].

Sulphate, acetate and perchlorate ions do not interfere in this method. Phosphate and nitrate ions in low concentrations do not interfere, however, in higher concentration they give erroneous results. The interferences of these ions were studied using corresponding acids. Zn^{2+}, Cd^{2+}, Bi^{3+}, Be^{2+} and Mg^{2+} do not interfere, however ions such as Tl^{4+}, As^{5+} and W^{6+} interfere strongly and must be absent.

Aluminium amalgam reduces ions chosen for the present study in 0.25*N* HCl or 0.5*N* H_2SO_4. It works efficiently and more rapidly than any of the hitherto used reductors. It is also cheaper than zinc, mercury or silver. However, the amalgam reacts with water and hence it should be prepared just before use. The column should be emptied immediately after use, otherwise the product of the reaction with water (i.e., Aluminium hydroxide) occupies more volume and hence the column breakes. The used amalgam may be washed free of acid with distilled water, blotted with filter paper and stored in a stoppered bottle for further use.

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Studies on Hydroxamic Acids. Part VI : Gravimetric Determination and Separation of Beryllium, Yitrium, Dysprosium and Erbium with N-*m*-Tolyl-*m*-Nitrobenzohydroxamic Acid

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A quantitative determination and separation of Be^{2+}, Y^{3+}, Tb^{3+}, Dy^{3+} and Er^{3+} in presence of various diverse ions was made by precipitation with N-*m*-tolyl-*m*-nitrobenzohydroxamic acid. The complexes having the composition $(C_{14}H_{11}N_2O_4)_nM$ were weighed directly after drying at 110°.

THE analytical potentialities and physico-chemical properties of N-*m*-tolyl-*m*-nitrobenzohydroxamic acid (N-*m*-T-*m*-NBHA)[1-8] reveals that it is a good complexing reagent. In continuation with our previous work[4-10] the further use of this reagent for separation and gravimetric determination of Be, Tb, Dy and Er is described.

Experimental

Chemicals :

All the chemicals used were of highest purity available.

Reagents :

A reagent N-*m*-tolyl-*m*-nitrobenzohydroxamic acid has been synthesised is described elsewhere[11] and 0.1% alcoholic solution was used for precipitation of metal ions.

The 0.001 *M* solution of metal ions were prepared and final concentration were determined volumetrically[12].

A 1% solution of masking agent (cyanide, oxalate, or Mg-EDTA) was prepared by dissolving the requisite amount in double distilled water.

Procedure :

In a litre beaker, 10 ml solution of metal ions (Be, Y, Tb, Dy, or Er) and about 500 ml distilled water were heated at 60° on water bath. The *p*H of precipitation was adjusted with ammonium acetate and acetic acid (Table 1). Then about 20 ml alcoholic solution of reagent (N-*m*-T-*m*-NBHA) was added dropwise with constant stirring followed by 0.01 solution of ammonium hydroxide until complete precipitation was obtained. The granular complexes thus obtained were digested for 20 min on water bath, filtered through fine porosity filter paper washed with first alcohol water mixture and then water and mounted on a steel planchette. The complexes were dried and weighed as $(C_{14}H_{11}N_2O_4)_nM$, (where M = Be, Y, Tb, Dy, or Er).

Results and Discussion

The *p*H of precipitations and the data on gravimetric determination for Be^{2+}, Y^{3+}, Tb^{3+}, Dy^{3+}, and Er^{3+} with N-*m*-tolyl-*m*-nitrobenzohydroxamic acid are given in Table 1. The data for separation are given in Tables 2-3.

TABLE—1 GRAVIMETRIC DETERMINATION OF Be^{2+}, Y^{3+}, Tb^{3+}, Dy^{3+} AND Er^{3+} WITH N-*m*-TOLYL-*m*-NITROBENZOHYDROXAMIC ACID

Compd. No.	Metal	*p*H of pption		wt. in mg.			
I	Be^{2+}	5.5-6.2	taken	0.09	0.18	0.36	1.80
			wt. of ppt	5.50	11.01	22.64	109.55
			found	0.09	0.18	0.37	1.79
II	Y^{3+}	5.5-6.5	taken	0.89	1.78	3.57	8.93
			wt. of ppt	9.05	18.08	36.30	90.40
			found	0.89	1.77	3.57	8.92
III	Tb^{3+}	9.0-9.5	taken	1.59	3.18	6.36	15.90
			wt. of ppt	9.78	19.50	38.88	97.85
			found	1.59	3.19	6.36	15.91
IV	Dy^{3+}	9.2-9.6	taken	[illegible]	2.43	8.10	16.20
			wt. of ppt	9.70	14.55	48.65	97.25
			found	1.61	2.42	8.10	16.19
V	Er^{3+}	9.5-10.0	taken	1.67	2.50	3.34	8.35
			wt. of ppt	9.80	14.65	19.60	48.95
			found	1.67	2.49	3.39	8.34

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TABLE—2 SEPARATION OF Be(II) FROM DIVERSE IONS

Be(II) taken mg	Diverse ions taken (mg)	Masking agents	Be(II) found mg
0.36	Ag^{+} (50)	Cyanide	0.86
0.86	Mn^{2+} (75)	Cyanide	0.86
0.86	Zn^{2+} (75)	Cyanide	0.86
0.86	Cd^{2+} (75)	Cyanide	0.87
0.86	Hg^{2+} (100)	Cyanide	0.87
1.86	Cu^{2+} (100)	Cyanide	1.88
1.86	Mg^{2+} (75)	Cyanide	1.84
1.86	Fe^{3+} (80)	Cyanide	1.85
1.86	Ga^{3+} (80)	Cyanide	1.86
1.86	Al^{3+} (80)	Mg-EDTA	1.87
1.86	V^{5+} (80)	Mg-EDTA	1.84
1.86	Mo^{6+} (100)	Mg-EDTA	1.85
1.86	Pb^{2+} (80)	NTA	1.85
1.86	Pd^{2+} (80)	NTA	1.86
0.36	Sn^{2+} (100)	NTA	0.86
0.86	Bi^{3+} (100)	NTA	0.36
0.86	Zr^{4+} (100)	NTA	0.37
1.86	Ti^{4+} (100)	NTA	1.86
1.86	La^{3+} (80)	NTA	1.86
1.86	Ce^{3+} (80)	NTA	1.86
1.86	Pr^{3+} (80)	NTA	1.85
1.86	Nd^{3+} (80)	NTA	1.85
1.86	Sb^{3+} (80)	IODATE	1.85
1.86	Th^{4+} (80)	a	1.86
0.36	U^{6+} (80)	a	0.37

a by adjusting pH ; NTA nitrilotriacetate

TABLE—3 SEPARATION OF Y(III), Tb(III), Dy(III) AND Er(III) FROM DIVERSE IONS

Metal ion taken : Y^{3+} 1.78 mg ; Tb^{3+} 3.18 mg ; Dy^{3+} 2.43 mg ; Er^{3+} 2.50 mg.

Diverse ions taken mg	Masking Agents	Metal ions found, mg Y^{3+}	Tb^{3+}	Dy^{3+}	Er^{3+}
Ag^{+} (50)	Cyanide	1.77	3.18	2.44	2.50
Mn^{2+} (75)	Cyanide	1.78	3.18	2.44	2.50
Zn^{2+} (75)	Cyanide	1.77	3.18	2.45	2.50
Cd^{2+} (75)	Cyanide	1.79	3.20	2.43	2.52
Hg^{2+} (100)	Cyanide	1.78	3.17	2.43	2.53
Cu^{2+} (100)	Cyanide	1.78	3.16	2 43	2.50
Mg^{2+} (75)	Cyanide	1.77	3.20	2.43	2.48
Fe^{3+} (80)	Cyanide	1.76	3.20	2.43	2.51
Ga^{3+} (50)	Cyanide	1.78	3.17	2.43	2.50
Pb^{2+} (80)	Citrate+oxalate	1.78	3.17	2.43	2.50
Sb^{3+} (80)	Citrate+oxalate	1.78	3.17	2.42	2.48
Pd^{2+} (80)	Citrate+oxalate	1.78	3.17	2.42	2.51
Sn^{2+} (100)	Citrate+oxalate	1.77	3.17	2.42	2.50
Bi^{3+} 9(100)	Citrate+oxalate	1.76	3.18	2.44	2.51
Zr^{4+} (100)	Citrate+oxalate	1.76	3.18	2.42	2.51
Ti^{4+} (80)	Citrate+oxalate	1.78	3.19	2.43	2.50
Al^{3+} (80)	Mg-EDTA	1.78	3.19	2.44	2.50
V^{5+} (80)	Mg-EDTA	1.78	3.19	2.43	2.50
Wo^{6+} (100)	Mg-EDTA	1.77	3.19	2.43	2.50
U^{6+} (80)	a	1.79	3.18	2.48	2.49
Th^{4+} (80)	a	1.79	3.18	2.43	2.49
La^{3+} (80)	a	1.79	3.18	2.44	2.49
Ce^{3+} (80)	a	1 78	3.18	2.42	2.50
Sm^{3+} (80)	a	1.78	3.18	5.42	2.50
Be^{2+} (80)	a	1.78	3.18	2.44	2.50

a by adjusting the pH

1. Separation of Be, Y, Tb, Dy, or Er from Common Metal Ions :

(*i*) *Using Masking Agents* : Into 10 ml of 0.001 *M* solution of Be, Tb, Dy, or Er with the desired foreign metal ions were and diluted to about 500 ml. Then 10 ml of 1% KCN solution was added and pH was adjusted. The contents were heated to 60°. The reagent solution was added dropwise with constant stirring. The complex thus formed was allowed to stand for about 20 min on water bath. It was filtered, washed, dried and weighed as before. The metals could be separated from and determined in the presence of Ag^{+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Cu^{2+}, Mg^{2+}, Fe^{3+} and Ga^{3+}.

Y, Tb, Dy, and Er could be separated from and determined in presence of Pb^{2+}, Pd^{2+}, Sb^{3+}, Sn^{2+}, Bi^{3+}, Zr^{4+} and Ti^{4+}, with 10 ml of 1% citrate and oxalate instead of cyanide solution. Be, Y, Tb, Dy and Er could be separated from Al^{3+}, V^{5+} and Mo^{6+} by using Mg-EDTA as a masking agent.

Be could be separated from Pb^{2+}, Pd^{2+}, Sn^{2+}, Bi^{3+}, Zr^{4+} and Ti^{4+} and La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, using nitrilotriacetate as masking agent. Be could also be separated from Sb^{3+} by masking with iodate.

(ii) *By adjusting pH* : 10 ml solution (0.001) of metal ion (Y,Tb,Dy or Er) was diluted to 500 ml and mixed with diverse ions. The Ag^{+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Al^{3+}, Th^{4+} and U^{6+} were precipitated below pH 5.5 using excess of reagent (N-*m*-T-*m*-NBHA). The precipitate was filtered, washed thoroughly and from mother liquor Y, Tb, Dy or Er was precipitated by adjusting the pH.

2. Characteristic of the Complexes :

The complexes are white in colour. They are freely soluble in dioxane, chloroform, toluene and fairly soluble in ethanol. These complexes were decomposed when treated with concentrated nitric, perchloric and sulphuric acids. The IR spectra and analytical results indicate that the composition of the complexes are $(C_{14}H_{11}N_2O_4)_3M$ (Table 4).

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TABLE—4

Copd. No.	Molecular weight Found	Molecular weight Calculated	IR spectra cm^{-1} $\nu C=O$	IR spectra cm^{-1} $\nu N=O$	Analysis % found C	found N	found M	calculated C	calculated N	calculated M
I	822.80	822.78	1565	918	61.34	10.22	1.09	61.31	10.25	1.10
II	902.60	902.68	1560	918	55.90	9.30	9.87	55.88	9.31	9.85
III	972.70	972.69	1550	915	51.85	8.62	16.84	51.86	8.64	16.34
IV	976.20	976.27	1555	915	51.65	8.62	16.65	51.67	8.61	16.64
V	981.00	981.03	1560	915	51.40	8.55	17.05	51.42	8.56	17.05

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2-Hydroxy-4-Methylacetophenone Oxime (HMAOX) as an Analytical Reagent : Studies on Palladium Chelate

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2-Hydroxy-4-methylacetophenone oxime (HMAOX) has been used as a reagent for gravimetric determination of palladium and for its separation from several cations and anions. Palladium is quantitatively precipitated by HMAOX between *p*H range 1.5-4.0. After drying the precipitate at 120°, its composition corresponds to the formula $Pd(C_9H_{10}O_2N)_2$. Interference due to copper(II) and titanium(IV) has been eliminated by masking with EDTA and NaF or KF respectively and in other cases by suitable control of *p*H.

DIFFERENT methods used for the gravimetric determination of palladium have been reviewed critically by Beamish[1]. Many orthophenolic oximes[2-6] have already been reported as analytical reagents for palladium. 2-Hydroxy-4-methylacetophenone oxime (HMAOX)[7] has now been successfully employed for the gravimetric determination of palladium, its separation from a number of ions and determination of palladium and nickel in their binary mixture.

The present work on the reaction of HMAOX with Pd(II) was undertaken with the intention to introduce a new ligand for the gravimetric determination of palladium. HMAOX gives yellow precipitate with palladium between *p*H range of 1.0 to 4.0.

Experimental

All the chemicals used were of A.R. Grade. Stock solution of palladium(II) was prepared by dissolving palladium chloride in A.R. HCl, diluting the solution and determining its Pd(II) content with dimethylglyoxime[9]. Solutions of other ions were prepared from samples of corresponding salts. An ethanolic solution of the reagent was employed and *p*H was adjusted using hydrochloric acid and sodium acetate.

Synthesis of the reagent :

2-Hydroxy-4-methylacetophenone[7] was obtained in almost quantitative yield by Fries migration of *m*-cresylacetate[8] in presence of anhydrous aluminium chloride. Its oxime[7] was prepared by the reaction of above ketone with hydroxylamine hydrochloride and potassium hydroxide (40%) in dilute ethanol. It was crystallised from petroleum, m.p. 102°.

Determination of palladium :

A known volume of palladium solution taken in a beaker was diluted to about 150 ml and the *p*H was adjusted to 2.0. The solution was warmed to 60-70° and a calculated volume of ethanolic solution of the reagent (1%) was added with constant stirring until no more precipitation took place on adding excess of the reagent solution. The precipitate was digested on water-bath for 30 min. It was then filtered hot through a sintered glass crucible (G_4), washed with hot water (60-70°) to remove foreign ions and the buffer adhering the precipitate. The precipitate was finally washed several time with 60 per cent ethanol to remove excess of the reagent. The precipitate was dried at 120° to constant weight. The metal content was determined using factor 0.2449. The results of some of the estimations are given in Table 1.

TABLE—1 DETERMINATION OF PALLADIUM(II)

Pd taken, (mg)	Wt. of complex, (mg)	Pd found, (mg)	Error (mg)
2.608	10.6	2.596	−0.012
9.780	39.9	9.772	−0.008
32.600	133.2	32.630	−0.030

Effect of pH :

Palladium was precipitated at different *p*H values adjusted with HCl and sodium acetate solutions maintaining all other conditions identical. The precipitation commenced at *p*H 1.0 and was quantitative between *p*H 1.5 and 4.0.

Determination of palladium in presence of foreign ions :

To study the effect of foreign ions on gravimetric determination of palladium, 20-25 mg of various cations as well as anions were added to a known vloume of Pd(II) solution (6.52 mg Pd) at *p*H 2.0 and estimations were carried out as mentioned above. Hg(II), Pb(II), As(III), Cd(II), Al(III), Mn(II), Zn(II), Co(II), Ni(II), Ba(II), Sr(II), Ca(II)

and Mg(II) were found not to form any insoluble complex with the reagent at *p*H below 3.5, hence they created no interference in the estimation of Pd(II) by the reagent at *p*H 2.0. Fe(III) ion which formed soluble complex with the reagent at lower *p*H was completely masked by adding tartaric acid (2.0 g) before adding the reagent. Cu(II), Ti(IV), vanadate and molybdate ions formed insoluble complexes[10] with the reagent at low *p*H and these ions interfere in the gravimetric determination of Pd(II). Interference due to Cu(II) was removed by masking with EDTA (0.5 g) before adding the reagent. Interference due to Ti(IV), vanadate and molybdate was removed by adding NaF or KF (0.5 g) as masking agent before adding the reagent. It was found that anions like tartarate, citrate, nitrate, fluoride do not interfere in the estimation of Pd(II).

Separation and determination of palladium and nickel :

Definite volume of standard solutions of palladium and nickel ions were mixed together and diluted to 200 ml. *p*H of solution was adjusted to 2.0. The yellow coloured palladium chelate precipitated was estimated gravimetrically as above. The filtrate and washings after the removal of palladium chelate were collected for the estimation of nickel. Its *p*H was adjusted to 5.5 using sodium acetate solution and nickel was estimated gravimetrically[11]. Some of the results given in Table 2 show that palladium and nickel can be accurately determined when present in the same solution.

TABLE—2 ESTIMATION OF PALLADIUM(II) AND NICKEL(II)

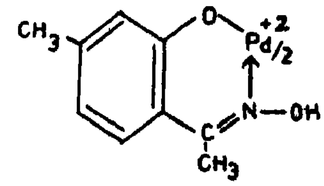
Metal taken (mg)		Wt. of Complex, (mg)		Metal found, (mg)		Error, (mg)	
Pd(II)	Ni(II)	Pd(II)	Ni(II)	Pd(II)	Ni(II)	Pd(II)	Ni(II)
2.608	3 0	10.6	19.7	2.596	2.990	+0.012	−0.01
13.04	18 0	58.0	118.5	12.98	17.99	−0.06	−0.01
26.08	30.0	106.7	197.0	26.13	29.90	+0.05	−0.10

Metal-ligand composition :

Direct conductometric titrations have been done to ascertain the palladium HMAOX ratio in palladium complex. Different volumes of the prepared $\frac{M}{50}$ Pd(II) solution were taken in beakers and in each beaker varying volumes of the prepared $\frac{M}{50}$ reagent solution and absolute alcohol were added in such a way that the total volume in each beaker remained 40 ml. The conductance of the solutions in each beaker were then determined. Graphs between the conductance against the volume of the reagent added for a fixed amount of palladium indicated 1 : 2 metal-ligand ratio for palladium complex.

The palladium chelate was analysed for its carbon, hydrogen and nitrogen content to determine the composition. The metal content was determined by standard analytical method (Found : C, 49.4 ; H, 4.4 ; N, 6.7 ; Pd, 24.32 ; Calc. C, 49.7 ; H, 4.6 ; N, 6.4 ; Pd, 24.49). The composition of chelate corresponds to the formula $Pd(C_9H_{10}O_2N)_2$ in which metal-ligand ratio is 1 : 2. The molecular weight determined cryoscopically using camphor as solvent showed the chelate to be monomeric, i.e., the chelate could be represented by ML_2. The 1 : 2 stoichiometry is confirmed by Job's method of continuous variation. The palladium complex was experimentally found to be diamagnetic, as expected.

On the basis of above results following structure is suggested to the metal chelate.



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Colorimetric Determination of Fenitrothion and Methyl Parathion using a Hydroxylaminolytic Procedure

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The liberation of *p*-nitro-*m*-cresol (PNC) and p-nitrophenol (PNP) from fenitrothion (o, o-dimethyl o-p-nitro-*m*-cresyl phosphorothionate) and methyl parathion (o, o-dimethyl o-p-nitrophenyl phosphorothionate) respectively by alkali alone is a slow process, but the rate can be increased many hundred fold by substituting alkali with a mixture of 0.5*N* sodium hydroxide and 0.67 *M* hydroxylamine. The reaction is almost instantaneous at room temperature when the system also contains 33 per cent. ethanol. Taking advantage of the above finding a procedure has been worked out for the spectrophotometric determination of fenitrothion and methyl parathion via the PNC and PNP liberated. The method is simple and quantitative and avoids the drastic chemical steps involved in the currently available methods. The sensitivity is about 0.1 μmole and the method can be used for the determination of the two insecticides in technical preparations, formulations and enzymic digests.

FENITROTHION (Sumithion, O,O-dimethyl O-*p*-nitro-*m*-cresyl phosphorothionate) and methyl parathion (O,O-dimethyl O-*p*-nitrophenyl phosphorothionate) are extensively used organophosphorurs insecticides. The former differs from the latter in containing a methyl group in the meta position of the *p*-nitrophenyl moiety. Yet the presence of this "magic methyl group" somehow confers on the insecticide a high degree of selectivity[1]. Whereas methyl parathion is equally toxic to both insects and mammals, fenitrothion is toxic to insects to the same extent as methyl parathion but is almost innocuous to mammals[2]. Because of this reason fenitrothion is in much demand for use on food crops. Several reasons have been postulated for this selectivity[3-5] based on the higher rate of detoxification of the compound in the mammalian system but the enzymes responsible have not been characterised.

We are interested in the metabolism of fenitrothion, and as a preliminary have developed a method for the extraction and determination of the residual fenitrothion and methyl parathion in enzymic digests. Whereas in the currently available procedures[6,7] the *p*-nitrocresol (PNC) and *p*-nitrophenol (PNP) moieties have to be liberated by refluxing with alcoholic potassium hydroxide, a mixture of hydroxylamine and alkali easily hydrolyses the compounds at room temperature in a very short period. Though the method is primarily developed for application in biochemical studies, it can be used in the assay of the two insecticides in technical preparations and formulations.

Materials and Methods

A Bausch and Lomb Spectronic 20 colorimeter was used with tubes of 1 cm light path. The samples of fenitrothion (95.4%) and methyl parathion (about 80%) were obtained through the courtesy of Bayer (India) Ltd., Bombay. Stock solutions containing 100 μ moles/ml (0.693 g of fenitrothion and 0.658 g of methyl parathion in 25 ml of ethanol) were prepared and preserved in the refrigerator. Other reagents were prepared as described previously[8,9]. The isobutanol-benzene mixture[10] used will be referred to as BB in the text. The calibration curves of PNP and PNC (obtained from the National Chemical Laboratory, Poona) drawn as described earlier[9] were found to be identical.

Determination of free PNC and PNP : One ml of fenitrothion stock solution (or the sample) is blown into about 90 ml of 0.1 *N* hydrochloric acid which also contains 1 ml of 10% (w/v) Triton X-100. The volume is adjusted to 100 ml with acid and the mixture is vigorously shaken to obtain a uniform suspension. The solution contains 1 μmole/ml of fenitrothion. In a separating funnel 10 ml of the suspension is shaken with 10 ml of BB for 1 min. The lower aqueons layer is discarded. The solvent layer is then gently shaken with 10 ml of 0.05 *N* sodium hydroxide which leaches out only the free PNC. The lower aqueous layer is filtered through a fluted filter paper and the absorbance determined at 410 nm. This value gives the free PNC in 10 μ mole of fenitrothion. The valus for free PNP in methyl parathion can be determined in a similar manner.

Determination of fenitrothion and methyl parathion : The BB layer from above is dried by shaking with about a gram of anhydrous sodium sulphate. Of this aliquots of 0.4 ml in triplicate are pipetted into test-tubes of approx 15 × 1.8 cm. The solvent is evaporated in an air-oven at 115±5°

(30-45 min). The tubes are then cooled to room temperature and 1 ml of ethanol added to each followed by 2 ml of freshly prepared (1+1) mixture of 3.5 *N* sodium hydroxide and 2 *M* hydroxylamine hydrochloride. After waiting for not less than 3 min the solution is diluted to 10 ml, filtered and the colour determined at 410 nm. The value can be read off from the standard graph wherein ethanol has been included. This value multiplied by 2.5 gives the fenitrothion content in 1 ml of the aqueous suspension. Methyl parathion is also determined as above. Technical preparations and formulations are treated as described for parathion[9]. In biochemical work, 10 ml of an enzymic digest is extracted with an equal volume of BB for the determination of free PNC or PNP and the un-reacted insecticide.

Results and Discussion

The results of the preliminary experiments which led to the development of the present method are given in Table 1. The experimental details are as

TABLE 1—RATE OF HYDROLYSIS OF FENITROTHION, FENITRO-OXON AND METHYL PARATHION TO PNC AND PNP IN VARIOUS MEDIA

(Half-lives were calculated from first order rate constants determined at 20°. Experimental details are as given in refs. 8 and 9. Average of 2 or more experiments)

Expt No.	Medium	Half-life in minutes: Fenitrothion	Fenitro-oxon	Methyl parathion
1.	0.5*N* NaOH aqueous	778	1.5	452
2.	0.5*N* NaOH – 33% ethanolic	198	1.7	41
3.	0.5*N* NaOH + 0.67*M* hydroxylamine – aqueous	23	Too rapid	1.2
4.	As above – 33% ethanolic	0.5 to 1.1	Too rapid	Too rapid
5.	0.5*N* NaOH, 33% ethanolic + 0.05*M* hydroxylamine	18		
6.	As above with 0.1*M* hydroxylamine	4.3		
7.	,, ,, 0.2*M* ,, ,,	2.0		
8.	,, ,, 0.3*M* ,, ,,	1.1		
9.	,, ,, 0.4*M* ,, ,,	0.9 to 1.1		

given for EPN (O-ethyl O-*p*-nitrophenyl phenylphosphonothioate)[8] and parathion[9]. It is seen that the half-life of fenitrothion in 0.5 *N* alkali which is 778 min at 20° is reduced nearly a thousand-fold in the presence of 0.67 *M* hydroxylamine and 33% ethanol. The reaction is almost instantaneous at room temperature (25-30°). There is a similar reduction in the half-life of methyl parathion. It is also seen that in the case of fenitro-oxon, the oxygen analogue of fenitrothion, the half-life is uniformly low with or without hydroxylamine. The fenitro-oxon was prepared by oxidation of fenitrothion by bromine water and the extent of conversion monitored as for parathion[11]. Experiments were also done with methyl paraoxon but the reaction rate was too rapid and the results are therefore not included in the table. Since the oxygen analogues are more rapidly hydrolysed than the thio compounds there is a possibility that the catalysis due to hydroxylamine may involve an intermediate step of conversion of the thio to the oxo form. To determine this, the degradation product of fenitrothion, viz., O, O-dimethyl phosphoric ester was isolated by extraction with a solvent from an acidic solution according to the principles given by Ramachandran[12]. The isolated substance was found to have the same R_f value as O, O-dimethyl phosphorothioate when chromotographed according to Plapp and Casida[13] and to be different from O, O-dimethyl phosphate which was the product isolated by hydrolysis of fenitro-oxon. The same thio compound was isolated during the degradation of methyl parathion. These results show that during the hydrolysis of fenitrothion and methyl parathion by hydroxylamine and sodium hydroxide the products formed are O, O-dimethyl phosphorothioate and PNC or PNP. This was further confirmed by qualitative tests on the phosphoric acid ester after sodium fusion when the presence of sulphur was confirmed.

The exact role of hydroxylamine in speeding the hydrolytic rate of fenitrothion, methyl parathion and other PNP-containing insecticides[8,9] is not clear, but expts 5-9 in Table 1 indicate that the reaction rate is dependent to some extent on the concentration of hydroxylamine. This is in agreement with the findings of Jandorf[14] who showed that hydroxylamine reacts with organophosphates like DFP (diisopropyl phosphorofluoridate) and sarin (O-isopropyl methyl phosphonofluoridate) in accordance with the following equation :

$$(RO)(R'O)P(O)X + 3NH_2OH \rightarrow (RO)(R'O)P(O)OH + N_2 + NH_3 + HX + 2H_2O$$

From this it is clear that the role of hydroxylamine is not merely catalytic but that it is actually taking part in the reaction.

It is now well documented that nucleophiles such as hydroxylamine, oxamate ions, hydrogen peroxide ions and O-Cl groups, which show common structural features of an electronegative atom with un-shared electrons alpha to the attacking atom, all exhibit reactivity towards phosphoryl phosphorus much greater than would be predicted from their basicities. This phenomenon has been referred to as "α-effect" by Edwards and Pearson[15], but the mechanism has not been fully understood. It is obvious that in the hydroxylaminolytic procedure developed in this paper the above effect is responsible for the accelerated rate of reaction. The spectacularly enhanced effect on the thio compounds as compared to the oxygen analogues is still not clear. In addition to the effect of hydroxylamine, the presence of ethanol seems to accelerate the reaction still further. The reason may be that alkoxide ions are more effective than hydroxide ions[16,17].

Certain quaternary oximes such as 2-pyridine aldoxime methiodide or methochloride (2-PAM) are effective antidotes against poisoning by organophosphorus insecticides[18]. Their antidotal effect

is due to their ability to make a nucleophilic attack on the phosphoric ester moiety after the organophosphate has formed a covalent bond via the serine hydroxyl group with the vital enzyme acetylcholinesterase. The phosphoric ester is thus detached and the enzyme reactivated. It may be mentioned that one of the early reactivators tried was hydroxylamine[19,20] which was, however, found to be considerably less effective than the quaternary oximes. We attempted a comparative study of the effectiveness of 2-PAM (which is an extensively used antidote against organophosphorus insecticide poisoning) and hydroxylamine on the rate of hydrolysis of parathion *in vitro*. The results are given in Table 2. It is seen that 2-PAM is very much less

TABLE 2—RATE OF LIBERATION OF *p*-NITROPHENOL FROM PARATHION WITH HYDROXYLAMINE AND 2-PYRIDINE ALDOXIME METHOCHLORIDE* AS CATALYSIS

(The media contained 0.5*N* NaOH and 33% ethanol in all cases. Half-lives were calculated from first order rate constants at 20°. Experimental details are as given in refs. 8 and 9)

Molar concn. of catalyst	Half-life in minutes in presence of Hydroxylamine	2-PAM
0.025	178	647
0.05	74	627
0.1	28	579
0.2	22	523
0.4	10	502
0.5	6	463
0.67	3.7	325

* A product of Aldrich Chemical Co., Inc., Milwaukee, Wis., USA.

effective than equimolar concentrations of hydroxylamine in the hydrolysis of parathion. Whereas, as a reactivator of phosphorylated acetylcholinesterase, 2-PAM is more effective than hydroxylamine, the reverse seems to be case with the hydrolysis of parathion itself. Obviously, in the case of the inhibited enzyme the quaternary ammonium group of 2-PAM helps by orienting the molecule before the oxime makes a nucleophilic attack on the P atom[18] while this is not possible in the case of the organophosphate itself.

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NOTES

Solid State Studies on Polymerization and Depolymerization of Tungstate ion with Tellurium as the Hetero Atom

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A new condensation inorganic polymer, $Na_8[TeW_{12}O_{40}]$ $24H_2O$, has been prepared and characterised on the basis of analytical and molecular weight determinations. The thermal depolymerization of the product has been studied extensively.

Of condensation inorganic polymers[1], no reports on 12 heteropoly tungstotellurate are found in the linterature. The present note is an attempt towards that line.

To 100 ml of aqueous solution of M/5 sodium tungstate, 20 ml of telluric acid was gradually added with constant stirring at a controlled temperature of 60° in a thermostat. After half an hour interval, glacial acetic acid was added dropwise to this solution till *p*H comes just in the range of 4.6 to 4.8. The solution was boiled constantly for 3 hrs., evaporated to half of its volume and allowed to crystallise in vacuo when bright needle-shaped crystalline compound came out which was washed with ethanol and recrystallised thrice from hot water. Analysis of the compound was carried out by the usual chemical methods and sodium was estimated by flame-photometric method (Found : Na, 1.45 ; Te 3.80 ; W, 78 ; H. 1.25%. Calcd. for $Na_8[TeW_{12}O_{40}]$ $24H_2O$: Na, 1.32 ; Te, 3.69 ; W, 63.90 ; H, 1.39%). Hydrogen has been analysed by element estimation method. From the analytical data, the molecular formula of the compound, as per Keggin's view[2], comes out to be $Na_8[TeW_{12}O_{40}]$ $24H_2O$.

Molecular Weight Determination : The cryoscopic method, as has been applied successfully by Alexander[3] and by Thilo and Kruger[4] for molecular weight determination of polymerised silicic acids, condensed phosphates, etc., in water and motten sodium sulphate decahydrate ; has also been applied here for the determination of the approximate molecular weight of the compound, in the same condition, i.e., in water and in motten sodium sulphate decahydrate[3,4]. This determination showed the molecular weight of the polymeric compound to be 3397 as compared with the calculated value 3451.91. To know the accurate degree of polymerization this result has been corroborated by X-ray crystal diffraction technique[2] for molecular weight determinations of heteropoly acid. The crystal diffraction data of the compound are $a=12.96$, $b=29.10$, $c=10.22$Å and $\alpha=\beta=\gamma=90°$, volume per unit cell 'V'$=3854.329$ Å^3, number of molecules per unit cell 'Z'$=2$. Pycnometric measurement gives the observed density 'ρ_{obs}'$=2.96$ gml^{-1}. From the relation $\rho_{obs} = \frac{1.66M.Z}{V}$, the molecular weight 'M' of the compound comes to 3436 against the calculated value 3451.91.

Thermal Depolymerization : The thermal depolymerization of the compound has been studied on the light of the investigations made by West and Audrieth[6] and by Babad-Zakhryapin on a few heteropoly tungstic acids. The apparatus used for this purpose was that described by Ray and Sinha[5] with continuous pumping the depolymerised product, followed by successive weighing using a thermogravimetric balance and estimations at some stages. The dissociation[5] of the compound was observed at 60° under reduced pressure when four molecules of water were eliminated. At 130° further twelve molecules of water were lost. The rest of the eight molecules of water remained intact in the crystal latice till 360°, above which they were completely removed. This work agreed cl osely with the work of Scroggie and Clark[9] with the comparable compounds. When the temperature was raised still higher, then nearly at 780°, the compound was broken as a whole into the basic units of lower oxides of tungsten and tellurium which has been confirmed by analysis. So the thermal stability of 12-heteropoly tungstotellurate is 780°. Comparing this thermal stability with that of heteropoly silicotungstic acids[6] and phosphotungstic acids[7], it may be concluded that the greater the positive charge in the central ion, $[W_{12}O_{40}]^{8-}$, the more effective is the binding in resulting heteropoly anion, stabilizing the latter against thermal vibrations and resultant decomposition.

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Copper(II) Complexes of Caffeine-Diacetato Bis Caffeine Copper(II)

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THE complexes of caffeine with copper nitrate and ruthenium chloride have recently been reported by Biagicingi et al[1] and Krentzien et al[2] respectively. The present communication reports on the preparation and characterisation of the copper(II) complex, viz. $[Cu(OAc)_2(caffeine)_2]$ with caffeine. The additional interesting aspect of this complex is its ability to initiate vinyl polymerisation (acrylamide), both photochemically and thermally (70°).

Experimental

The complex was isolated by mixing methanolic solutions of caffeine and copper acetate, in the molar ratio of 2 : 1. The mixture was mechanically stirred at 60° for 90 minutes. The hot contents were then concentrated and crystallised. Bluish green crystals were filtered off, washed with acetone and ether and dried in vacuo.

The complex was analysed for copper content volumetrically. On analysis, the % of Cu, C, H and N are determined to be 10.58%, 40.53%, 4.36%, and 18.9% respectively and the calculated values are 10.81%, 40.82%, 4.42% aud 19.05% respectively for the formula $CuC_{20}H_{26}N_8O_8$.

Hilger-Watts Uvispec spectrophotometer for absorbance measurements, Perkin-Elmer infracord spectrophotometer for ir spectra, Gouy's magnetic balance for magnetic susceptibility, Philips conductivity bridge type PR 9500 for conductivity and Beckmann Freezing Point apparatus for molecular weight measurements were used.

NMR spectra were obtained in DMSO-d_6 with the Brucker NMR spectrophotometer (TMS as internal reference). The sweepwidth was 500 HZ and the sweeptime 500 sec.

Results and Discussion

The molar conductance in methanol at $10^{-3}M$ concentration shows the complex to be a non-electrolyte (11 mhos). The observed magnetic moment of 1.84 B.M. at 300°K for the complex, indicates the presence of one unpaired electron. These data, along with the molecular weight determination in DMSO solution (Found 565 ; calculated 570) suggest the monomeric structure for the complex.

Electronic Spectra :

The variations in different solvents (Table 1) together with the location of the absorption bands at not very high frequency possibly suggest a tetragonally distorted octahedral structure for the complex[8].

TABLE 1—ELECTRONIC SPECTRAL DATA FOR THE COPPER(II) COMPLEX

Solvent	Absorption bands in kK	
H_2O	39.00	18.50^{br}
CH_3OH	39.10	14.00^{br}
DMSO		14.50^{br}
CH_3CN		15.00^{br}

Ir Spectra :

In the ir spectra of the complex, the ν_{Cu-N} observed at 272 cm^{-1} bears similarity to the ν_{Cu-N} reported in the various copper-imidazole complexes[4]. The symmetric and antisymmetric vibrations of the OCO group which occur at 1420 cm^{-1} and 1580 cm^{-1} respectively, indicate the asymmetric bidentate nature of the acetato group.

NMR Spectra :

In caffeine, the PMR absorptions for the three -N-CH_3 groups appear at $\delta = 4.1$, 3.6 and 3.4. The only aromatic proton in the five membered ring of caffeine shows itself at $\delta = 7.6$. In the NMR spectrum of the complex, the above three methyl proton signals are not only shifted to lower field, but also broadened with the result that they merge to form a single new peak at $\delta = 3.31$. Further, the co-ordination of the N_9 atom of caffeine to the peramagnetic Cu^{2+} ion results in the broadening of the signal at 7.6 so much that it is no longer observed in the complex as supported by the work of Li et al[5,6,7]

Composition of the Complex :

Lambert Beer's law is obeyed by the complex within the concentration range 50 to 300 ppm. Job's continuous variation method indicated the formation of a 1 : 2 complex.

From the experimental methods described above, we conclude that caffeine behaves as an unidentate ligand with co-ordination to the metal atom through N_9 atom and that the complex can be represented by a tetragonally distorted octahedral structure with asymmetric chelation of the acetato group. This complex seems to be the second reported instance

wherein the dimeric structure of copper acetate has been destroyed[8].

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Mixed-ligand Complexes of Diamine (salicylato) Cu(II) and Diamine(salicylato) Ni(II) with 2-hydroxyacetophenone or 2-hydroxy-1-naphthaldehyde

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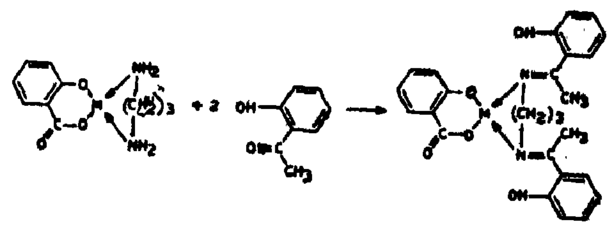
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A survey of the literature[1-8] has revealed that no work has been done on the mixed-ligand complexes of diamine(salicylato) Cu(II) and diamine (salicylato) Ni(II) with 2-hydroxyacetophenone or 2-hydroxy-1-naphthaldehyde. The present note deals with the mixed-ligand (Schiff base) complexes, synthesised by the interaction of 2-hydroxyacetophenone or 2-hydroxy-1-naphthaldehyde with the mixed complexes of the type [ML-1, 3 diaminopropane], where LH_2 = salicylic acid. The resulting mixed-ligand complexes retain (L^{-2}) in their structure while the $-OH$ groups of the Schiff base N-N'-propylene bis(α-methyl, 2-hydroxybenzylidene imino) or N-N'-propylene bis(2-hydroxy-1-naphthaledene imino) remain unco-ordinated.

The metal salicylates were treated with ethylene diamine or propylene diamine and the diamine (salicylato) Cu(II) and diamine(salicylato) Ni(II) obtained by the following two procedures :

(1) To a mixture of equimolar (1 *M*) aqueous solution of nickel chloride and salicylic acid in the ratio of 1 : 2, an aqueous solution of 1, 3-diamino propane (1 *M*) was added till the *p*H was ~6. After 40-45 minutes a greenish-blue precipitate was obtained. It was filtered, washed, dried, weighed and analysed. (2) Alternatively bis or tris-(1, 3-diamino propane) nickel(II) chloride (0.5 g) was dissolved in the minimum quantity of water and to it an aqueous solution of salicylic acid (1 *M*) was added till *p*H 6 was attained. After 40 minutes or so a greenish-blue compound obtained, was filtered, washed, dried, weighed and analysed. These compounds gave satisfactory C, H, N and metal analysis and based on these data their composition (Fig. 1) may be expressed by [MLA] $2H_2O$, where M = Cu(II) or Ni(II), LH_2 = salicylic acid and A = ethylenediamine or propylene diamine.



[MLA]$2H_2O$ [MLSB]

Fig. 1. Mixed-ligand Complexes of Diamine (Salicylato) M(II) with 2-Hydroxyacetophenone.

The analysis of the diamine(salicylato) metal(II) indicate them to be the mixed complexes. The water molecules associated with them are lost at 130° suggesting them to be either co-ordinated or water of crystallisation.

These mixed complexes were treated with 2-hydroxyacetophenone or 2-hydroxy-1-naphthaldehyde so that the two $-NH_2$ groups of the co-ordinated diamine molecule undergo condensation as described below.

A requisite quantity (0.5 g) of the mixed complex was refluxed with 10.0 ml of 2-hydroxyacetophenone or 2-hydroxy-1-naphthaldehyde on a water-bath for 3 hours. The solution was concentrated and the mixed-ligand complex was rendered insoluble by adding an excess of ether in which the unreacted 2-hydroxyacetophenone or 2-hydroxy-1-naphthaldehyde dissolved. The mixed-ligand complex was recrystallised from chloroform. Elemental analysis and molecular weight determinations give the formula [ML-SB] for these compounds, where SB stands for N-N' propylene bis(2-hydroxy-1-naphthalidene or N-N' propylene bis(α-methyl-2-hydroxy benzylidene).

The magnetic susceptibility measurements of the mixed-ligand complexes (Fig. 1) suggest the diamagnetic nature of the Ni(II)-complexes[4] and paramagnetic nature to the extent of one unpaired electron for the Cu(II)-complexes[8] (1.82 B. M.) at room temperature.

The electronic absorption spectra of the mixed complexes in water and mixed-ligand complexes in chloroform gave absorption peaks in the range of 300-950 nm.

The mixed-ligand copper(II) complexes in chloroform gave a broad absorption band at 500 nm suggesting their square-planar geometry. The mixed-ligand nickel(II) complexes gave two bands at ~420 nm and 510 nm and in no case absorption bands beyond 600 nm were observed which indicate the square-planar geometry of the complexes.

The negligibly small values ($\triangle$ M = 5.0 − 7.8 × ohm^{-1} cm^{2} $mole^{-1}$) of molar-conductance of the mixed-ligand complexes in chloroform suggest them to be neutral in nature. The I.R. spectra indicate a broad band in the range 3600-3200 cm^{-1} suggesting that the −OH groups are unco-ordinated.

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Viscosity of NaCl, NaBr and $NaNO_3$ in Dioxane-Water Mixtures at Different Temperatures

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THE variation of viscosity with temperature and solvent compositions has been employed to study the ion-solvent interaction by many workers[1] both in aqueous and non-aqueous solutions. In the present communication an attempt has been made to deal with the ion-solvent interaction of NaCl, NaBr and $NaNO_3$ in dioxane-water mixtures of varying compositions to see the effect of temperature and hydrogen bonding on the B-coefficient of the viscosity equation. The activation energy and the entropy of activation of the viscous flow of these solutions have also been calculated for interpreting the influence of strong electrolytes upon the viscosity of the solvent as a rate process.

All the salts used were of E. Merck 'extra pure varieties. The samples were recrystallised, dried at 180° and kept in vacuum. Preparation of the solvent, solutions and procedure for measurement were the same as described earlier[2].

The Jones-Dole equation[1] has been found to be adequate as the plot of η_r-1/$C^{\frac{1}{2}}$ vs $C^{\frac{1}{2}}$ is found to be linear. This is in contrary to that of the results of P. K. Das[3] who has used an empirical equation : $\eta_r = 1 + AC^{\frac{1}{2}} + BC^{x}$, where 'x' is an empirical constant without any physical significance. The constant B of the Jones-Dole equation which is regarded as a measure of the ion-solvent interaction could be calculated, from the slope of the above plot, are tabulated in Table 1. The B value increases in case of NaCl and $NaNO_3$ with increase in temperature whereas it is irregular in case of NaBr. The plot of 'B' vs 't' is linear for NaCl and $NaNO_3$ whereas it is a curve for NaBr.

Nightingale[4] has suggested the B value as a measure of ion-dipole interaction. Dioxane is more or less a non-hydrogen bonded solvent. So the ion-dipole interaction energy in the absence of any hydrogen bond energy would be appreciable and the attachment of the solvent molecules to the ions may not be loose and hence no structure formation would occur in the solvents around the ion[5]. The net result will be stronger solvation and more ion-solvent interaction.

Proceeding in the similar manner as that of Nightingale[6] et al, the energy of activation $\triangle$E, free

TABLE —1

Temp. in °C.	B/l. mol⁻ NaCl 10%D	NaCl 20%D	NaCl 30%D	NaBr 10%D	NaBr 20%D	NaBr 30%D	$NaNO_3$ 10%D	$NaNO_3$ 20%D	$NaNO_3$ 30%D
30	0.081	0.1002	0.1554	0.0971	0.1200	0.1510	0.071	0.0955	0.1802
35	0.091	0.1122	0.1662	0.1150	0.1240	0.1700	0.085	0.01085	0.1420
40	0.1400	0.1500	0.2000	0.0661	0.1122	0.1445	0.1020	0.1148	0.1580
45	0.1500	0.1620	0.2200	0.0648	0.1080	0.1120	0.1120	0.1250	0.1600

TABLE—2

	10%D			20%D			30%D		
	ΔE in K cals	ΔF in K cals	ΔS in E.U.	ΔE in K cals	ΔF in K cals	ΔS in E.U.	ΔE in K cals	ΔF in K cals	ΔS in E.U.
Solvent	4.084	2.290	5.82	4.158	2.491	5.41	4.022	2.580	6.63
NaCl	4.221	2.308	5.97	4.358	2.571	5.70	4.292	2.710	6.79
NaBr	3.852	2.260	5.62	4.048	2.361	5.61	3.894	2.457	6.49
$NaNO_3$	3.899	2.263	5.70	4.086	2.371	5.28	3.911	2.506	6.51

energy of activation ΔF and entropy of activation ΔS have been computed at 35° and recorded in Table 2. For this calculation our own viscosity data for dioxane-water mixtures have been used. It is observed that the energy and entropy of activation of viscous flow in case of NaCl is greater than that of the solvent whereas it is less in case of NaBr and $NaNO_3$. The large energy and entropy of activation are attributed to the excess of energy necessary to break the hydrogen bonds in solutions, i.e., for NaCl. In case of bromide and nitrate structure is broken down at all solvent compositions. From Table 2, it is seen that that the ion-solvent interaction is of the order $Br^- > NO_3^- > Cl^-$ and is in agreement with that of Kay[7], who distinguished between the structure breaking and structure making ions by plotting $\Delta(\lambda^\circ \eta_r)/\Delta T$ vs $\Delta B \frac{1}{2} \Delta T$.

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Optical Resolution of (±) α-(o, m-carboxyphenylamino)-Arylacetonitriles

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α-Aminonitriles being the most important intermediates for the synthesis of amino acids, we have prepared[1-4] a number of them of type (±) $R-C_6H_4-CH(CN)-NH-R'$, where R = –OH or $-OCH_3$, R' = *o*- or *m*-carboxyphenyl groups. We reported here the optical resolution of α-(*o* or *m*-carboxyphenylamino)-*m* or *p*-hydroxyphenyl or *p*-methoxyphenyl acetonitrile into their enantiomers through their brucine salts. The optical rotations measured in different solvents showed that the introduction of hydroxy group in α-(*m*-carboxyphenylamino)-phenylacetonitrile decreases the absolute value of optical rotation while that of methoxy group in α-(*o*-carboxyphenylamino) phenylacetonitrile increases the optical activity.

Experimental

Resolution of (±) α-(o-carboxyphenylamino)-p-methoxyphenylacetonitrile

A clear solution of (±) α-(*o*-Carboxyphenylamino)-*p*-methoxyphenylacetonitrile[3] (5.64 g) and (–)-brucine (7.29 g) in hot acetone (70 ml) on cooling for 72 hrs. deposited a crystalline salt, *crop-A* (6.5 g), m.p. 130-32°. On two further crystallisations from a mixture of acetone and chloroform, *crop-A* yielded *crop-C* (1 g), m. p. 138°. The latter on decomposition yielded the optically pure (+)-nitrile, m.p. 150-51°, $[\alpha]_D + 70°$. Further crystallisations did not increase the optical rotation.

The mother liquor was concentrated to get *crop-A'* (6.5 g) m.p. 118-20°, part of which was decomposed to (–)-nitrile $[\alpha]_D - 23°$ (C = 1.5). On two further crystallisation from a mixture of acetone and chloroform it gave *crop C'* (1 g) m.p. 134° which on decomposition gave (–)-nitrile, m.p. 148° $[\alpha]_D - 40°$. The rotation did not increase on further crystallisation.

Resolution of (±)-α-(m-Carboxyphenylamino)-m-hydroxyphenylacetonitrile :

A clear solution of (±)-α-(*m*-carboxyphenylamino)-*m*-hydroxyphenylacetonitrile[4] (10.72 g) and (–)-brucine (15.58 g) in hot acetone (200 ml.) was subjected to fractional crystallisations as above. The fully active (+)-nitrtle, m.p. 155°, $[\alpha]_D + 20°$ and (–)-nitrile, m.p. 154-55°, $[\alpha]_D - 20°$ were obtained.

Resolution of (±)-α-(m-Carboxyphenylamino)-p-hydroxyphenylacetonitrile :

(–) Brucine (11.8 g) was added to (±)-α-(*m*-carboxyphenylamino)-*p*-hydroxyphenylacetonitrile[4]

TABLE—1

OPTICAL ROTATIONS OF α-AMINONITRILES* OF THE TYPE (+) AND (–) $R-C_6H_4-CH(CN)-NH-R'$ IN DIFFERENT SOLVENTS†

Solvent	R = *p*-methoxy, R' = *o*-carboxyphenyl				R = *m*-hydroxy, R' = *m*-carboxyphenyl				R = *p*-hydroxy, R' = *m*-carboxyphenyl			
	(+) isomer		(–) isomer		(+) isomer		(–) isomer		(+) isomer		(–) isomer	
	conc	$[\alpha]_D$	conc	$[\alpha]_D$	conc	$[\alpha]_D$	conc	$[\alpha]_D$	conc	$[\alpha]_D$	conc	$[\alpha]_D$
Acetone	1.0	+70.0	0.5	–40.0	0.7	+20.0	0.8	–20.0	1.0	+15.0	1.1	–18.0
Ethanol	1.0	+68.0	0.7	–38.0	1.0	+18.0	0.7	–15.0	1.1	+12.0	1.2	–15.0
Methanol	0.7	+60.0	0.8	–35.0	1.2	+15.0	1.0	–12.0	1.2	+10.0	1.0	–15.0
Dioxane	0.8	+58.0	1.0	–38.0	1.1	+12.0	1.1	–12.0	1.2	+10.0	1.3	–12.0
Ethylacetate	0.8	+70.0	1.1	–40.0	1.0	+20.0	1.2	–18.0	1.1	+15.0	1.2	–17.0

* All the isomers gave correct N analysis.
† All the optical rotations were measured at 23°. (l = 1)

(8.05 g) in hot acetone (150 ml). The clear solution of brucine salt on two fractional crystallisations gave (–)-nitrile, m.p. 178°, $[\alpha]_D - 18°$ (c=1.2) and (+)-nitrile, m.p. 176° $[\alpha]_D + 15°$.

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Synthesis of Some 4-Hydroxybromoquinoline-3-Carboxylic Acids

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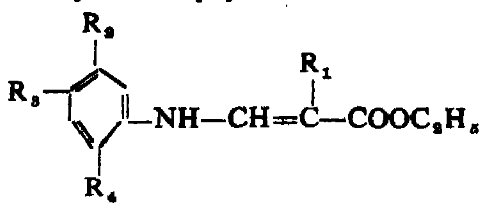
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In continuation of our previous work[1,2] attempts were made to apply the acetic anhydride-sulphuric acid method to cyclise acrylates prepared by condensing ethyl ethoxymethylene-malonate or-cyanoacetate with 5-bromo-*o*-toluidine, 3-bromo-*p*-toluidine, 4 : 6-dibromo-*m*-toluidine, 4-bromo-*o*-anisidine and 4-bromo-*o*-phenetidine. Since the yields of the cyclised products obtained with this method were poor due to the decomposition of the acrylates resulting in the formation of bromacetarylanilides, the acrylates were cyclised by the thermal method of Price and Roberts[3].

Table—1

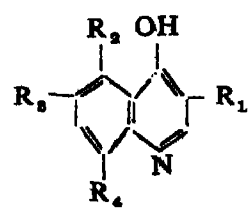
Arylaminoacrylates R_1 = $-COOC_2H_5$ or $-CN$



	R_2	R_3	R_4	R_1'	Yield %	m.p.s.	R_1'	Yield %	m.p.s
1.	H	Br	CH_3	$-COOC_2H_5$	77	106°	$-CN$	76	195°
2.	H	CH_3	Br	,,	83	86	,,	96	192
3.	CH_3	Br	Br	,,	75	Sticky	,,	51	225
4.	Br	H	OCH_3	,,	84	118	,,	31	140
5.	Br	H	OC_2H_5	,,	93	105	,,	37	173

Table—2

4-Hydroxyquinolines



	R_2	R_3	R_4	(a) R_1	Yield %	m.p.s	(b) R_1	Yield %	m.ps.	R_1	Yield % a	Yield % b	m.p.s.
1.	H	Br	CH_3	$-COOC_2H_5$	77	310	$-CN$	94	330° dec.	$-COOH$	78	41	301° dec.
2.	H	CH_3	Br	,,	88	262	,,	61	360	,,	68	75	360 ,,
3.	CH_3	Br	Br	,,	27	305	,,	84	300 dec.	,,	72	39	277 ,,
4.	Br	H	OCH_3	,,	52	295	,,	28	200	,,	87	34	290 ,,
5.	Br	H	OC_2H_5	,,	Sticky		,,	19	291 dec.	,,	19.5	56	281

Experimental

Ethyl bromarylaminomethylene-malonates & -cyanoacetates :

Ethyl bromarylaminomethylene-malonates were prepared by the method of Duffin and Kendall[4] from the appropriate bromarylamine and ethyl ethoxymethylene-malonate by heating the mixture at 110° and the corresponding cyanoacetates by the method of Snyder and Jones[5] by heating the mixture of the arylamine, ethyl cyanoacetate and ethyl orthoformate at 160-165° and the acrylates were purified by the usual treatment (details vide Table 1).

3-Carbethoxy- and 3-cyano-4-hydroxybromoquinolines :

Ethyl bromarylaminomethylene-malonate (15 g) or cyanoacetate (10 g) was cyclised to corresponding quinoline in boiling diphenyl ether (150 cc) and the product crystallised from ethanol or acetic acid (Table 2).

4-hydroxybromoquinoline-*3*-carboxylic acids :

3-Carbethoxyquinolines were hydrolysed by refluxing with 2N ethanolic sodium hydroxide for 3 hours and the 3-cyanoquinolines with an aqueous mixture of sulphuric and acetic acids (each 25 cc). Neutralisation of the basic or acidic solution gave the corresponding carboxylic acids (Table 2) which were purified by repeated alkali and acid treatment. The mixed m.p.s of corresponding acids in both cases did not show any depression.

Elemental analysis of (N) & (Br) were found to be within ±4% of the theoretical value for all the compounds prepared.

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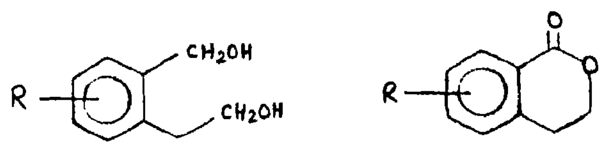
Chromic Acid Oxidation of Some Substituted 2-Hydroxymethylphenethyl Alcohols

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2-Hydroxymethylphenethyl alcohols have been shown[1-4] to be transformed into their corresponding isochroman-1-ones through the respective isochromans. Substituted 2-Hydroxymethylphenethyl alcohols(I) could now be directly oxidised to isochroman-1-ones(II) with chromic acid in one step following the procedure of Kubota *et al*[5]. Also, IIf was converted to IIa by catalytic hydrogenation over Pd/C and subsequent treatment with diazomethane.



I II

Ia, $R = 4,5\text{-di-}OCH_3$ — IIa, $R = 6,7\text{-di-}OCH_3$
Ib, $R = 5,6\text{-di-}OCH_3$ — IIb, $R = 5,6\text{-di-}OCH_3$
Ic, $R = 4,6\text{-di-}OCH_3$ — IIc, $R = 5,7\text{-di-}OCH_3$
Id, $R = 4,5\text{-}O_2CH_2$ — IId, $R = 6,7\text{-}O_2CH_2$
Ie, $R = 4\text{-}CH_3\text{-}6\text{-}OCH_3$ — IIe, $R = 5\text{-}OCH_3\text{-}7\text{-}CH_3$
If, $R = 4\text{-}C_6H_5CH_2O\text{-}5\text{-}OCH_3$ — IIf, $R = 6\text{-}OCH_3\text{-}7\text{-}C_6H_5\text{-}CH_2O$

Experimental

6,7-Dimethoxyisochroman-1-one : A solution of CrO_3(0.3 g) in water (0.6 ml) and glacial AcOH (2 ml) was added dropwise with stirring to 2-hydroxymethyl-4,5-dimethoxyphenethyl alcohol (I ; 0.2 g) dissolved in the same acid (6 ml). The temperature was maintained at 20-22° by occasional external cooling. After stirring for 0·5 hr. at the room temp., it was treated with an equal volume of water, extracted with $CHCl_3$ (2×25 ml), the extract washed with 2*N* Na_2CO_3, water and dried over any. Na_2SO_4. A dark yellow solid left after solvent evaporation was dissolved in dry benzene. It was chromatographed through a column of Brockmann alumina (30 g) and eluted with the same solvent. An almost colourless solid obtained was crystallised from ethylacetate-pet. ether (b.p. 60-80°) as colourless needles (0.07 g), m.p. 140-141°, undepressed on admixture with an authentic sample of the compound prepared earlier by a different route[3].

The following compounds were prepared by the method described above and crystallised from ethyl acetate-pet. ether unless otherwise mentioned.

5,6-Dimethoxyisochroman-1-one[1], m.p. 70-71° (37.5% yield) was purified by sublimation (bath temp. 90-95°/0.1 mm) followed by crystallisation from ethyl acetate.

5,7-Dimethoxyisochroman-1-one[3], colourless needles, m.p. 97-98° (35% yield).

6,7-Methylenedioxyisochroman-1-one[1], colourless prisms, m.p. 126-27° (25% yield).

5-Methoxy-7-methylisochroman-1-one[4], cubes, m.p. 79-80° (yield 42% yield).

6-Methoxy-7-benzyloxyisochroman-1-one[5], yellow shining flakes, m.p. 125-26° on trituration with pet. ether (yield 50%) was debenzylated by catalytic hydrogenation over Pd-C and subsequently treated with diazomethane to furnish 6-methoxy-isochroman-1-one, 139-40°.

Acknowledgement

The authors wish to express their gratitude to Prof. A.B. Lal, Head of the Department of Chemistry for providing research facilities. They are also grateful to Dr. K. D. Banerji for his kind advice and co-operation.

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Synthesis of 2, 6-Diaryl-5 : 6-Dihydro-4H-1 : 3-Thiazines

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SEVERAL diversely substituted 2, 6-Diaryl-5 : 6-dihydro-4H-1 : 3-thiazines are synthesized using method of Giordano et al[1,2], and their structures confirmed by elemental analysis, infra-red spectra and in few cases mass spectra. These (Table 2) were prepared by condensation of N(Hydroxymethyl)-thiobenzamides[3] (Table 1) and styrenes in acetic acid.

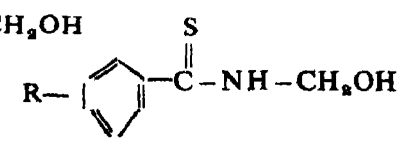
Experimental

N-Hydroxymethyl Thiobenzamides: These were prepared by heating a mixture of thiobenzamides (0.02 mole), 200 ml. water, 20 ml. 40% formaldehyde (0.5 mole) on a water bath for 15-30 minutes. Contents were cooled and extracted with ether, ether stripped off after drying to get title products (vide Table 1).

2, 6-Diaryl-5 : 6-Dihydro-4H-1 : 3-Thiazines: To a stirred solution of N-Hydroxymethyl-thiobenzamide (0.045 mole) and styrene (0.045 mole) in glacial acetic acid (70 ml) was added conc. sulfuric acid (0.045 mole) dropwise so as to maintain the reaction mixture around 15°. After addition, stirring at this temperature was maintained for six hours and mixture left overnight at room temperature. It was then poured onto crushed ice and basified with 40% aq. sodium hydroxide keeping temp. ~ 10°. The solution was now extracted with ether, ether

Table—1

$R-C_6H_4-C(S)NH.CH_2OH$

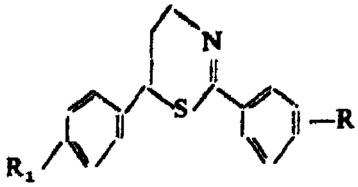


Phenyl-substituted-N-hydroxymethyl-thiobenzamides

No.	R	M.P. °C.	% age yield	Molecular Formula	%N Found	%N Calcd	%S Found	%S Calcd
1.	2.	3.	4.	5.	6	7	8	9
1.	H	65[a]	91	C_8H_9NOS	—	—	—	—
2	p-CH_3	86	88	$C_9H_{11}NOS$	7.64	7.73	17.60	17.67
3.	p-OCH_3	84	88	$C_9H_{11}NO_2S$	6.99	7.10	16.11	16.24
4.	p-Cl	90-91[b]	87	C_8H_8ClNOS	—	—	—	—
5.	p-Br	69	84	C_8H_8BrNOS	5.63	5.69	13.00	13.02
6.	3 : 4-Methylenedioxy.	92	78	$C_9H_9NO_3S$	6.55	6.63	15.15	15.17

a. Reported by H. Böhme, and H. H. Hotzel, *Arch. Pharm.* 1967, **300**, 241,
b. Reported by C. Giordano, *Synthesis*, 1972, No. 1, 34-35.

TABLE—2



2, 6-DIARYL-5, 6-DIHYDRO-4H-1, 3-THIAZINES

No.	R	R_1	M.P./B.P. °C.	HCl M.P., °C.	Molecular Formula	%N Found	%N Calcd	%S Found	%S Calcd
1	2	3	4	5	6	7	8	9	10
1.	H	H	86-87[a]	—	$C_{16}H_{15}NS$	—	—	—	—
2.	p-CH_3	H	110[a]	—	$C_{17}H_{17}NS$	—	—	—	—
3.	p-OCH_3	H	65	—	$C_{17}H_{17}NOS$	4.84	4.95	11.22	11.31
4.	p-Cl	H	96[a]	—	$C_{16}H_{14}ClNS$	—	—	—	—
5.	p-Br	H	91-92	—	$C_{16}H_{14}BrNS$	4.13	4.22	9.58	9.64
6.	3, 4-Methylenedioxy.	H	107-108	—	$C_{17}H_{15}NO_2S$	4.61	4.71	10.69	10.77
7.	-H	$-CH_3$	103-105/760 mm.	84	$C_{17}H_{17}NS.HCl$	4.54	4.62	10.50	10,56
8.	p-CH_3	$-CH_3$	242-760 mm	76	$C_{18}H_{19}NS.HCl$	4.34	4.41	10.04	10.09
9.	p-OCH_3	$-CH_3$	239-41/760 mm	70	$C_{18}H_{19}NOS.HCl$	4.10	4.21	9.55	9.60
10.	p-Cl	$-CH_3$	228/760 mm	62	$C_{17}H_{16}ClNS.HCl$	4.07	4.14	9.41	9.47
11.	p-Br	$-CH_3$	236/760 mm	89-90	$C_{17}H_{16}BrNS.HCl$	3.54	3.66	8.31	8.37
12.	3, 4-Methylenedioxy.	$-CH_3$	78-80	—	$C_{18}H_{17}NO_2S$	4.38	4.50	10.19	10.29
13.	-H	$-OCH_3$	85	—	$C_{17}H_{17}NOS$	4.85	4.95	11.23	11.31
14.	p-CH_3	$-OCH_3$	230/760 mm	80	$C_{18}H_{19}NOS.HCl$	4.11	4.21	9.54	9.60
15.	p-OCH_3	$-OCH_3$	239-40/760 mm	78	$C_{18}H_{19}NO_2S.HCl$	3.92	4.01	9.09	9.16
16.	p-Cl	$-OCH_3$	227/760 mm	76	$C_{17}H_{16}ClNOS.HCl$	3.86	3.97	8.99	9.04
17.	p-Br	$-OCH_3$	237-38/760 mm	81	$C_{17}H_{16}BrNOS.HCl$	3.40	3.52	7.96	8.04
18.	3, 4-Methylenedioxy.	$-OCH_3$	88-89	—	$C_{18}H_{17}NO_3S$	4.16	4.28	9.70	9.79
19.	-H	-Cl	227/760 mm	82-83	$C_{16}H_{14}ClNS.HCl$	4.22	4.33	9.84	9.88
20.	p-CH_3	-Cl	230-31/760 mm	93-95	$C_{17}H_{16}ClNS.HCl$	4.05	4.14	9.40	9.47
21.	p-OCH_3	-Cl	232/760 mm	80-81	$C_{17}H_{16}ClNOS.HCl$	3.88	3.97	8.98	9.04
22.	p-Cl	-Cl	213/760 mm	88	$C_{16}H_{13}Cl_2NS.HCl$	3.81	3.91	8.90	8.93
23.	p-Br	-Cl	226/760 mm	82-84	$C_{16}H_{13}BrClNS.HCl$	3.39	3.48	7.88	7.94
24.	3, 4-Methylenedioxy.	-Cl	76	—	$C_{17}H_{14}ClNO_2S$	4.13	4.23	9.59	9.66

[a]. Reported by C. Giordano, Synthesis, 1972, No. 1, 34-35.

solution washed with $2N$ HCl (2×50 ml) at $\sim 10°$ and acid extract made alkaline by 40% aq. alkali. This was extracted with ether and after drying ethereal solution, it gave on evaporation thiazines (vide Table 2). If the product was liquid, it was isolated as hydrochloride. Yields were in the range of 30 to 50%.

I.R. Spectra of all these thiazines show absorption band at 1634-1600 cm^{-1} typical of C=N linkage present in dihydro-1, 3-thiazines as reported earlier[4]. Mol. Weights of first three were checked by their mass spectra.

Acknowledgement

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Synthesis of 3-Phenylsulphonamido-4-methoxybenzoic Acid Hydrazide and their Derivatives

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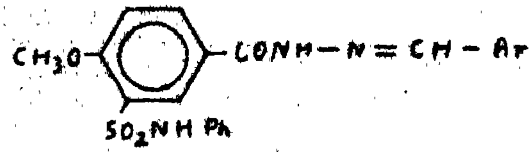
Manuscript received 7 May 1977; accepted 3 October 1977

IN continuation of the work done by us on hydrazides and their derivatives as antibacterial agents[1,2] we extend the work to 3-phenylsulphonamido-4-methoxybenzoic acid hydrazide. The hydrazide was synthesised and various N-benzylidene derivatives were prepared by condensing it with aromatic aldehydes. Condensation of the hydrazide with isothiocyanates yielded the thiosemicarbazides which were cyclised to 3,4-disubstituted-5-mercapto-1,2,4-4H triazole[3].

Experimental

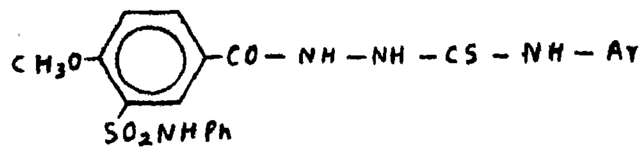
3-Chlorosulphonylamisic acid was prepared in 64% yield by the chlorosulphonation of anisic acid using 6 moles of chlorosulphonic acid at 65-70°[4], m.p. 178°[5]. (Found : C, 38.44 ; H, 3.0 ; S, 12.58 ;

TABLE 1—N-BENZYLIDENE-3-PHENYLSULPHONAMIDO-4-METHOXYBENZOIC ACID HYDRAZIDE



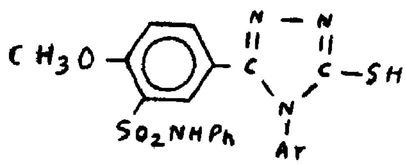
No.	Ar	M.P. °C	% Yield	Molecular Formula	% Analysis N Found	N Reqd.	S Found	S Reqd.
1.	C_6H_5	268	75	$C_{21}H_{19}O_4N_3S$	10.50	10.27	7.95	7.82
2.	2-HOC_6H_4	291	70	$C_{21}H_{19}O_5N_3S$	9.91	9.88	7.59	7.53
3.	4-HOC_6H_4	287	78	$C_{21}H_{19}O_5N_3S$	9.79	9.88	7.68	7.53
4.	4-$CH_3OC_6H_4$	308	79	$C_{22}H_{21}O_5N_3S$	9.77	9.67	7.38	7.29
5.	4-$NO_2C_6H_4$	283	67	$C_{21}H_{18}O_6N_4S$	12.30	12.33	6.98	7.05
6.	4-OH-3-$OCH_3C_6H_3$	273	62	$C_{22}H_{21}O_6N_3S$	9.38	9.23	7.10	7.03
7.	2-Furyl	284	65	$C_{19}H_{17}O_5N_3S$	10.20	10.52	8.35	8.02

TABLE 2—1-(3′-PHENYLSULPHONAMIDO-4′-METHOXYPHENYL) AROYL-4-ARYL THIOSEMICARBAZIDE



No.	Ar	M.P. °C	% Yield	Molecular Formula	% Analysis N Found	N Reqd.	S Found	S Reqd.
8.	4-BrC_6H_4	217	91.5	$C_{21}H_{19}O_4N_4S_2Br$	10.5	10.47	12.03	11.96
9.	4-$CH_3C_6H_4$	208	85.0	$C_{22}H_{22}O_4N_4S_2$	12.0	11.91	13.66	13.61
10.	4-Cl C_6H_4	209	89.0	$C_{21}H_{19}O_4N_4S_2Cl$	11.32	11.43	13.17	13.06
11.	1-Naphthyl	161	81.0	$C_{25}H_{22}O_4N_4S_2$	11.1	11.07	12.71	12.65

TABLE 3—3-(3′-PHENYLSULPHONAMIDO-4′-METHOXYPHENYL)-4-ARYL-5-MERCAPTO-1, 2, 4-4H TRIAZOLE



No.	Ar	M.P. °C	% Yield	Molecular Formula	% Analysis N Found	N Reqd.	S Found	S Reqd.
12.	4-BrC_6H_4	275	86	$C_{21}H_{17}O_3N_4S_2Br$	11.00	10.83	12.31	12.38
13.	4-$CH_3C_6H_4$	263	84	$C_{22}H_{20}O_3N_4S_2$	12.48	12.39	14.18	14.16
14.	4-Cl C_6H_4	281	87	$C_{21}H_{17}O_3N_4S_2Cl$	11.80	11.87	13.41	13.56
15.	1-Naphthyl	291	77	$C_{25}H_{20}O_3N_4S_2$	11.45	11.48	13.00	13.12

Cl, 14.0%. Calcd for $C_8H_7O_5SCl$; C, 38.31 ; H, 2.79 ; S, 12.8 ; Cl, 14.2%).

3-Phenylsulphonamido-4-methoxybenzoic acid was prepared using molar amounts of aniline with pyridine as a base m.p. 235° (crystallised from ethanol) yield 66% (Found : C, 54.2 ; H, 4.35 ; N, 4.55 ; S, 10.48%. Calcd. for $C_{14}H_{13}O_5NS$: C, 54.73 ; H, 4.23 ; N, 4.56 ; S, 10.42%).

The methyl ester m.p. 176° (crystallised from ethanol) yield 78% (Found : C, 55.91 ; H, 4.80 ; N, 4.30 ; S, 10.2%. Calcd. for $C_{15}H_{15}O_5NS$: C, 56.08 ; H, 4.67 ; N, 4.36 ; S, 9.97%), and the hydrazide m.p. 108° (crystallised from ethanol) yield 83% (Found : C, 52.19 ; H, 4.61 ; N, 13.0 ; S, 10.03%. Calcd. for $C_{14}H_{15}O_4N_3S$: C, 52.34 ; H, 4.67 ; N, 13.08 ; S, 9.97%) were prepared in the usual manner.

The N-benzylidene derivatives (Table 1), 1-(3′-phenylsulphonamido-4′-methoxyphenyl)-aroyl-4-aryl thiosemicarbazide (Table 2) and 3-(3′-phenylsulphonamido-4′-methoxyphenyl)-4-aryl-5-mercapto-1, 2, 4-4H triazoles (Table 3) were prepared in the usual manner[4].

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Chemical Constituents of *Polypodium amoenum* Wall

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POLYPODIUM amoenum (Polypodiaceae) grow in the Himalayan region at an altitude 4,000-11,000 ft and also from Garhwal to Bhutan, very common in Khasia range (altitude 3,000-6,000 ft). The present communication describes the isolation of fern-9(11)-ene[1-3], hop-22(29)-ene[4-6] and β-sitosterol from the whole plant.

Benzene extract of the dried powdered fern was separated into acid and neutral fractions. The latter was chromatographed over alumina. Elution with petrol (60-80°) yielded a waxy solid which was found by TLC (12% $AgNO_3$ impregnated silicagel) to be a mixture of two components. On rechromatography over silicagel (E. Merck) impregnated with $AgNO_3$ followed by crystallisation (chloroform : methanol) it afforded two hydrocarbons A and B having the same mol. formula $C_{30}H_{50}$(M^+410).

Compound A (found C, 88.01, H, 12.15) m.p. 166-68° $[\alpha_D]^{CHCl_3}$ – 16.1° showed significant peaks at m/e 257, 243, 231 in its mass spectrum similar to those recorded for fern-9(11)-ene. Its identity was established by comparison with an authentic sample (m.m.p, IR and Co-TLC).

Compound B (found C, 87.59, H, 12.42), m.p. 210-11°, $[\alpha_D]^{CHCl_3}$ +61°. ν_{max}^{nujol} 880 cm^{-1} (>C=CH_2) was found to be identical (m.m.p, IR, MS) with hop-22(29)-ene (Diploptene).

Further elution of the column with petrol : benzene (3 : 2) furnished β-sitosterol, m.p. 133-36°, $[\alpha_D]^{CHCl_3}$ – 32°, acetate, m.p. 126-28°, $[\alpha_D]^{CHCl_3}$ – 38°, identical with authentic specimens.

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Coumarins from *Pimpinella diversifolia*

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P. *diversifolia* (Umbelliferae) is a herb growing in the north-western Himalayan region. No work on this plant has so far been reported. From the aerial parts of this plant two coumarins have been isolated and identified as ammirin (isoangenomalin) and oxypeucedanin on the basis of IR, NMR, MS and TLC data.

The petroleum ether extract of the air dried, powdered aerial parts (2 Kg) of the plant yielded a dark green residue (30 g) which was chromatographed over neutral alumina (grade IV). Elution with petroleum ether gave a mixture of hydrocarbons, m.p. 77-78°. The earlier benzene eluates on chromatography over silica gel followed by PLC afforded ammirin (44 mg) in needles (benzene-acetone), m.p. 110-12° (lit[a]. m.p. 117°), blue fluorescence under UV. NMR (90 MHz, $CDCl_3$) : δ 1.79(3H, *s*, methyl), 3.27 (2H, *dq*, *J* 16, 8Hz, H-3'), 4.98(1H, *br s*) and 5.13 (1H, *br s*)-oelefinic protons, 5.32 (1H, *t*, *J* 8Hz, H-2'), 6.23 (1H, *d*, *J* 9.5 Hz, H-3), 6.78 (1H, *s*, H-8), 7.30 (1H, *s*, H-5), 7.62 (1H, *d*, *J* 9.5 Hz, H-4). MS : Ion peaks at *m/e* 228 (M^+), 213, 185 among others.

Later fractions of benzene eluates from silica gel chromatography, on purification by PLC, afforded oxypeucedanin (20 mg), m.p. 144-45° (lit.[a] m.p. 142-43°), M^+ 286. IR and NMR spectra were in concordance with those of an authentic sample.

Acknowledgement

We thank Dr. Sukh Dev of Malti Chem. Research Centre, Baroda for the NMR spectra.

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Spectrophotometric Determination of Cobalt with Furoin Thiosemicarbazone@

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NUMEROUS reagents have been reported for the spectrophotometric determination of cobalt which include 1-nitroso-2 naphthol and thiocyanate[1], benzamidoxime[2], metidan[3] and thioglycerol[4]. Recently thiosemicarbazones of picolinaldehyde[5] and di-2 pyridylketone[6] are reported as reagents for the determination of various metal ions such as cobalt, nickel, iron and copper. The reported methods either require elaborate experimental procedure or complexes are less stable in aqueous medium. In this paper we propose furoin thiosemicarbazone as a new spectrophotometric reagent which has considerably high stability in aqueous medium. The procedure is simple and the interference due to several ions may be easily removed.

Experimental

Reagent

Ethanolic 10% solution of furoin (5 m mole) and aqueous 20% solution of thiosemicarbazide (20 m mole) were mixed in presence of 2-3 drops of anhydrous acetic acid and refluxed for two hours. The yellowish crystals of furoin thiosemicarbazone appeared on cooling were recrystallized twice from hot (1 : 1) ethanol.

0.25% (w/v) solution of furoin thiosemicarbazone was prepared in (1 : 1) methanol. The reagent solution is stable for at least two months.

Cobalt solution

A stock solution (1 mg ml^{-1}) of cobalt(II) ion was prepared by dissolving cobalt sulphate heptahydrate in double distilled water and was standardized gravimetrically[7].

Reagent grade chemicals were used throughout.

Beckman DU-2 spectrophotometer with 10 mm matched glass cuvettes was used for measuring the absorbance. *p*H was monitored with Philips PR 9405L *p*H meter with glass and calomel electrodes. *p*H values of the solutions were adjusted by dil. hydrochloric acid or ammonia solutions.

General procedure

An aliquot of sample solution containing up to 10 ppm of cobalt was taken and excess (20 times) reagent was added. The *p*H was adjusted to 7.5 and the solution was diluted to 25 ml in standard flask with distilled water. The optical density of the cobalt complex was measured at 365 nm against reagent blank prepared in the same manner excluding cobalt. The concentration of cobalt in the unknown solution was found out from standard calibration curve obtained under identical conditions.

Results and Discussion

Investigation of the spectra

The spectra of furoin thiosemicarbazone : cobalt systems were run over a wide range of *p*H values which show an absorption band with λ max at 365 nm. The extinction coefficient at 365 nm and at *p*H 7.5 is 8095 l mol^{-1} cm^{-1} (Fig. 1).

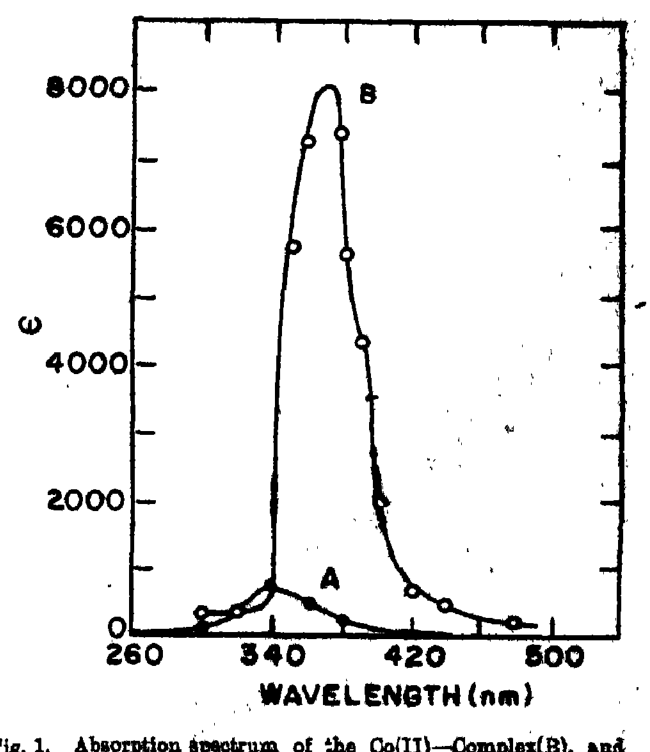


Fig. 1. Absorption spectrum of the Co(II)—Complex(B), and the ligand (A)

(B) : Co(II) : 6.792×10^{-5} *M* and ligand : 6.887×10^{-5} *M*

(A) : Ligand : 6.887×10^{-5} *M*

@ Paper presented to the Annual Convention of Chemists, Bangalore 1976.

Beer's law and physical constants

Beer's law was valid up to 10 ppm of cobalt. The Sandell sensitivity of the reaction as calculated from Beer's plot is found to be 0.00727 μg Co cm^{-2} at 365 nm for log Io/I = 0.001. The molar extinction coefficient of the complex is 8095 l mol^{-1} cm^{-1}. The Ringbom's plot indicated that the optimum range is 1.6 to 5.0 μg Co ml^{-1}.

Effect of pH

A series of solutions varying in *p*H from 3 to 12 were prepared and the absorbances were recorded at 365 nm. It was observed that no change in absorbance took place over the *p*H range 7 to 8. The absorbance of the solutions decreases at higher or lower *p*H values. The *p*H 7.5 was maintained in further studies.

Effect of reagent concentration

It was observed that 0.75 ml of the reagent solution is adequate for colour development. However twice the amount was used to ensure full colour development. The reagent has negligible absorbance at the wavelength selected for measurement.

Composition of the complex

Job's method of continuous variation[8] was studied. Solutions were mixed in different proportions keeping the total molarity constant. The curve obtained indicates the formation of cobalt complex in which the metal : ligand ratio is 1 : 2. This conclusion is supported by the mole ratio[9] and slope ratio[10-11] methods.

Effect of diverse ions

The solutions containing known amounts of cobalt and varying amounts of diverse ions were prepared and cobalt was determined in their presence. It was observed that large number of cations such as Tl^{3+}, UO_2^{2+}, Mo^{6+}, Zn^{2+}, V^{5+}, Ba^{2+}, Sr^{2+}, Cd^{2+}, Re^{6+}, Ce^{3+}, Cr^{3+}, Pb^{2+}, In^{3+} can be tolerated in the ratio of at least 1 : 20. Fairly large number of anions like SO_4^{2-}, $S_2O_3^{2-}$, HCO_3^-, $HCOO^-$, $HC_2O_4^-$, tartrate are tolerated in large amounts. Nickel ion shows strong interference and must be absent. Interference of copper can be avoided by prior separation[12]. Fluoride ion can be used as masking agent for Mn(II) and Fe(III) up to 30 ppm.

Acknowledgement

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Oxazine Dyes as New Iodometric Indicators*

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IN a continuation of our work on the use of oxazine dyes as indicators[1-4], we have found that eight oxazine dyes, Capri Blue(CPB), Meldola's Blue (MB), Celestine Blue(CLB), Gallamine Blue(GB), Solochrome Prune AS(SPAS), Brilliant Cresyl Blue (BCB) (Colour Index Nos. 51015, 51175, 51050, 51045, 51040 and 51010 respectively), Cresyl Fast Violet Acetate(CFVA), and Resazurin(RSZ) (the structures of these dyes are given below), can be used as indicators in the direct and reverse titrations of iodine with thiosulphate, arsenic(III), ascorbic acid, hydrazine, mercaptoacetic acid and uric acid. The advantages of these indicators are : their solubility in cold water and stability of their aqueous solutions. In this connection, it may be mentioned that till now very few indicators have been reported for the titration of ascorbic acid[5-8] and hydrazine[8] with iodine, and apart from starch, no other indicator has been proposed for the uric acid-iodine titration[9].

The indicator methods now developed have been utilised for the determination of ascorbic acid content of commercial vitamin C tablets and some fruit

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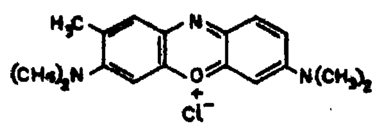
juices, as well as the determination of uric acid content of human urine.

Experimental

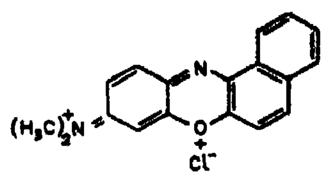
$0.1N$ solutions of iodine (in 2% KI solution), sodium thiosulphate, hydrazine sulphate, mercapto-acetic acid, ascorbic acid (EDTA was used as stabiliser) and $0.025N$ uric acid (1 g of uric acid+0.7 g of lithium carbonate in 500 ml water) were prepared and standardised. $0.1N$ arsenic(III) solution was also prepared.

the solution with $0.1N$ (or $0.01N$) sodium thiosulphate solution. The colour changes at the end points are : green to blue with CPB and BCB, light pink to violet with MB and CFVA, orange-red to pink with CLB, GB and SPAS and green to violet (orange-red to pink in titrations with ascorbic acid and mercaptoacetic acid) with RSZ.

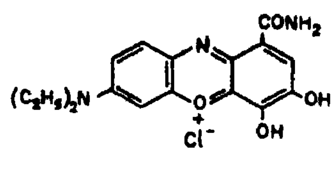
The same procedure can be employed using arsenic(III), ascorbic acid, hydrazine sulphate, mercaptoacetic acid or uric acid in place of sodium thiosulphate, provided, 0.5-1.0 g of sodium bicarbonate is added to the titration mixture while titrating



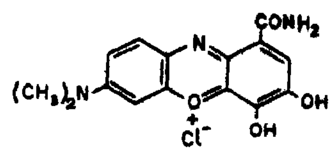
Capri Blue
(Colour Index No. 51015)



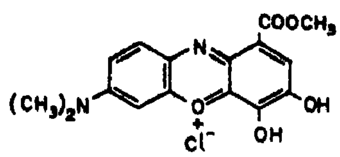
Moldola's Blue
(Colour Index No. 51175)



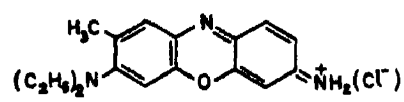
Celestine Blue
(Colour Index No. 51050)



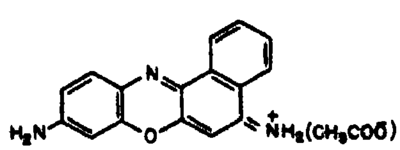
Gallamine Blue
(Colour Index No. 51045)



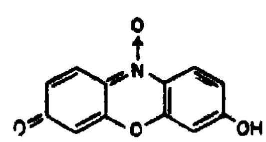
Solechrome Prune As
(Colour Index No. 51040)



Brilliant Cresyl Blue
(Colour Index No. 51010)



Cresyl Fast Violet Acetate



Resazurin

0.1% solutions (0.2% in the case of GB) of the dyes were prepared from the following dye samples : CPB, MB, SPAS and CFVA : Gurr ; CLB and GB : Chroma ; BCB : E. Merck ; RSZ : Baird & Tatlock (London) Ltd.

General Procedure : Transfer 3-10 ml of $0.1N$ (or $0.01N$) iodine solution ($0.025N$ in the case of titrations with uric acid) into a 250 ml iodine flask, dilute to 50 ml and add 0.1 ml of 0.1% CPB, MB, or BCB or 0.2 ml of 0.1% CLB, SPAS or CFVA or 0.2 ml of 0.2% GB or 0.05 ml of 0.1% RSZ, and titrate

with arsenic(III) and hydrazine sulphate solutions. Titrations with uric acid have to be conducted in presence of 2-3 g of sodium bicarbonate.

The results obtained by this method are in excellent agreement with those obtained by other methods.

Results and Discussion

Mechanism of indicator action : While discussing the use of Neutral Red, an azine dye, as indicator in the titration of iodide with silver nitrate, Sierra

and Asensi Mora[10] have stated that the colour change at the end point was due to the formation of a compound between Neutral Red and iodine. Since the eight dyes of the present investigation are very closely related to Neutral Red, we believe that a similar mechanism is operative in the iodometric titrations now reported. That is, a compound is formed between the dye and iodine and at the end point, thiosulphate, arsenic(III), etc., react with the compound and regenerate the dye. In this connection, it may be mentioned that Gautier[11] has proposed a similar mechanism in his studies on the use of the thiazine dye, Methylene Blue, as an iodometric indicator and spot test reagent for the detection of arsenic(III), thiosulphate, etc.

Determination of ascorbic acid content in commercial vitamin C tablets and fruit juices : Substances like maltose, lactose, dextrose, citric acid, tartaric acid, succinic acid, maleic acid, malic acid and mandelic acid do not interfere in the iodometric titration of ascorbic acid using the present oxazine dye indicators. Consequently, the determination of ascorbic acid content in commercial vitamin C tablets is carried out in accordance with the method of Rao and Prasad[8] employing 0.025*N* iodine solution and any one of the afore-mentioned dyes as indicator. The data presented in Table 1 show that the results obtained by the present indicator method are in excellent agreement with those obtained by the B.P. method[12].

TABLE—1 ESTIMATION OF ASCORBIC ACID IN COMMERCIAL VITAMIN C TABLETS

Trade name & manufacturer	*Ascorbic acid found, mg*	
	B.P. method	*Present method*
Suckose, IDPL	580±2	583±2
Redoxon, Roche	505±2	508±2
Celin, Glaxo	485±2	487±2
Chewcee, Lederle	511±2	513±2

Attempts for the estimation of ascorbic acid content of some fruit juices yielded satisfactory results with only Capri Blue and Brilliant Cresyl Blue as indicators ; with other indicators, the colour changes at the end points are not sharp. The results obtained with Capri Blue and Brilliant Cresyl Blue as indicators are in very good agreement with those obtained adopting the method given by Jacobs[13] as is evident from Table 2.

In these titrations, 0.025*N* iodine solution should be used as titrant and the titration should be carried out rapidly, as otherwise, the results obtained will not be accurate.

Determination of uric acid in human urine : The iodometric method for the determination of uric acid, using the indicators now proposed, can be applied for the determination of uric acid in human urine. The uric acid in the urine is precipitated as the ammonium salt, the ammonium salt dissolved in the minimum amount of 10% acetic acid and the resulting solution is titrated with iodine using the oxazine dye indicators, after adding 2 ml of saturated sodium bicarbonate solution. The results obtained are incorporated in Table 3.

TABLE—2 ESTIMATION OF ASCORBIC ACID CONTENT OF SOME FRUIT JUICES

Fruit		*Ascorbic acid in 100 ml of juice, mg*	
Common name	*Botanical name*	*Jacob's method*	*Present method*
Tomato	*Lycopersicum esculentum*	85.6±0.2	86.1±0.2
Lemon	*C. aurantifolia* (christm)	29.5±0.2	30.4±0.2
Orange	*C. aurantium* L	46.2±0.2	46.6±0.2
Batavia	*C. sinensis* (L) Osbeck	95.9±0.3	95.9±0.3
Grape	*Vitis vinifera*	12.3±0.2	12.2±0.2

TABLE—3 ESTIMATION OF URIC ACID IN HUMAN URINE

Sample No.	*Volume of urine, ml*	*Uric acid, mg*	
		Danet's method[14]	*Present method*
1	10.0	4.9±0.1	4.9±0.1
2	10.0	4.0±0.1	4.0±0.1
3	10.0	4.5±0.1	4.5±0.1
4	10.0	4.2±0.1	4.2±0.1

Reverse titrations : The reverse titrations, i.e., titrations of sodium thiosulphate, arsenic(III), ascorbic acid, hydrazine, mercaptoacetic acid and uric acid, with iodine, can be performed in 0.1*N* and 0.01*N* solutions, using the eight oxazine dyes as indicators, under the same conditions of direct titrations. The colour changes at the end points are just the reverse of those obtained in the direct titrations. In titrations of 0.1*N* solutions, no blank correction is necessary but while employing 0.01*N* solutions, the following blank corrections (of 0.01*N* iodine solution) should be applied : CPB and BCB : 0.02 ml ; MB and RSZ : 0.08 ml ; CLB, GB and SPAS : 0.04 ml. The colour change with CFVA is not satisfactory.

Acknowledgement

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New Indicators for Titrimetric Determination of Fluoride by Ferric Chloride

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THIOCYANATE[1], sodium salicylate[2] and resacetophenone oxime[3] have been investigated as indicators for the titrimetric determination of fluoride. Many other indicators like alizarin red[4], methyl thymol blue[5], xylenol orange[6], Na-rhodizonate[7], Na-purpurin-3-sulphonate[8] have been tried for its volumetric estimation. Even 4(2-pyridylazo) resorcinol has been studied for its titrimetric determination by various workers[9-10]. 5-alkoxy-2-nitrosophenols have been prepared[11,12] in the laboratory and used as chelating agents for bivalent metal ions. This article reports the use of these compounds as indicators for the titrimetric determination of fluoride with acidic ferric chloride solution.

Experimental

A stock solution of $0.1M$ sodium fluoride was prepared by dissolving 2.1 g of NaF in 500 ml of distilled water. $0.05M$ ferric chloride solution was prepared by dissolving 6.7575 g of ferric chloride hexahydrate in 500 ml of $0.01M$ HCl, 1% solutions of the pure samples of 5-methoxy-2-nitroso phenol, 5-ethoxy-2-nitroso phenol and 5-propoxy-2-nitroso phenol were prepared by dissolving required quantity in 95% ethanol. These solutions are fairly stable and give yellow colour with fluoride ion and very low concentration is required for the titration.

An aliquot of sodium fluoride solution was taken in a 100 ml conical flask. About 2.0 g of NaCl was added to it. The contents were shaken thoroughly well and then equal volume of 95% ethanol was added to it, which was followed by the addition of 0.2 ml. (4 drops) of 1% indicator solution. It was then titrated against $0.05M$ acidic ferric chloride of pH 1.5 at room temperature. The end point is marked with a sharp change of yellow to red colour.

It was found that the presence of 50 times excess of Cl^-, Br^-, NO_3^- and SO_4^{2-} was tolerated in this estimation of the fluoride.

It is evident from the results that the fluoride can be determined satisfactorily by the use of 5-alkoxy-2-nitroso phenols as indicators, even when the fluoride content is very low. These compounds are found to be efficient indicators because they form less strong complexes with ferric(III) rather than iron fluoride complex.

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The Influence of Different Frequencies of Laser on the Microbial Production of Alcohol by *Saccharomyces cerevisiae*

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THE applications of laser to study of biological system have been reviewed by many workers[1-3]. Both stimulating[4,5] and inhibitory[6-8] effects of laser on living organisms particularly on enzyme systems have been found. Combined effects of laser and some chemicals on living cells have also been explored[9,10]. But a little or no work to study the effect of laser on the fermentations has been done as yet.

The present investigation was undertaken with a view to improve the fermenting capacity of *Saccharomyces cerevisiae*.

Experimental

The culture medium (MY 20 Agar)[11] for 33 culture tubes for the growth of yeast was prepared. The *p*H of the medium was adjusted to 5 by lactic acid. About 5 ml of this medium was taken in each culture tube. The culture tubes were plugged with cotton and sterilized at 15 lb pressure for 30 minutes. After sterilization the culture tubes were kept in slanting position for a night. Then they were inoculated with fresh culture of yeast and incubated for 48 hrs at 30°. Soon after the growth of yeast was obtained, the tubes numbering 1 to 16 were irradiated by lower frequency (output at power 1 mW) of laser for 1, 5, 10, 20, 40, 80, 100, 120, 140, 180, 240, 360, 480, 600, 900 and 1800 seconds respectively. Similarly the culture tubes numbering 17 to 32 were irradiated by higher frequency (output at power 35 mW) of laser. Spectra Physics Model 125 A He—Ne Laser was used. The irradiated portion of the colony only was studied under the microscope to observe the mutation of the cells concerned as was evinced by their increasing size. These cells were isolated by pour plate technique and the isolated pure culture mutants so obtained were then used for the study of alcoholic fermentation. The remaining one out of 33 cultures was not exposed to laser and this was maintained as control.

These laser irradiated cultures are maintained in De's Culture Collection, Chemical Laboratories, University of Allahabad, Allahabad. The strain of *Saccharomyces cerevisiae* was borrowed from Mamfordganj distillery, Allahabad.

For alcoholic fermentation the medium was prepared by dissolving 1180.0 g market sugar, 29.7 g each of malt extract and yeast extract, 47.5 g peptone in 5 litres of distilled water. The *p*H of the medium was adjusted to 5 by lactic acid. The volume of the medium was noted and it was divided into 99 equal parts. Each part of the medium was taken into a separate 250 ml conical flask. The total volume of the medium present in each flask was raised to 100 ml by distilled water. The flasks were sterilized at 15 lb pressure for 30 minutes and cooled to room temperature. Then all the 99 flasks were arranged into 33 sets, each comprising 3 flasks. The flasks of set no. 1 were inoculated with five drops of yeast cell suspension of *S. cerevisiae* treated with lower frequency of laser for 1 second only. Sets 2 to 16 were also inoculated each with five drops of respective yeast suspension prepared from *S. cerevisiae* exposed to lower frequency of laser for 5, 10, 20, 40, 80, 100, 120, 140, 180, 240, 360, 480, 600, 900 and 1800 seconds respectively. Similarly sets 17 to 32 were inoculated with the respective yeast suspension prepared from *S. cerevisiae* exposed to different doses of higher frequency of laser. The remaining 33rd set was inoculated with yeast suspension belonging to control culture.

All the sets were then incubated at 30° for 72 hrs. After incubation alcohol produced was estimated colorimetrically[12].

Results and Discussion

The microscopic examination of yeast cells irradiated with different doses of higher frequency of laser showed that at 10 seconds exposure there was an appreciable increase in the size (8.4×4.8μ) and at 40 seconds exposure there was very high rate of budding. Higher doses (80 and 100 seconds), however, caused reduction in size (4.8×2.4μ) as compared to the parent strain (6.0×2.4μ). At these doses yeast cells were usually found to be oval or spherical in shape similar to the parent strain, while at other doses they were elongated. There was, in general, no effect of irradiation of lower frequency of laser on the morphology of yeast cells.

It was observed that barring a few higher doses (600, 900 and 1800 seconds) at all other doses of lower frequency of laser the amount of alcohol produced (Table 1) was found to be comparatively better than the control. The maximum increase in the yield was 36.9% in comparison to the control. The effect of higher frequency of laser (Table 2) on the production of alcohol was very encouraging. However, its higher doses were found to be detrimental in effect. The optimum yield (more than control by 97.4%) was obtained at 10 seconds dose. The minimum value (less than the control by 81.3%) was obtained at 1800 seconds dose. The effect of different doses of laser in respect of its stimulation on alcohol formation seems to be related to the level of energy present in them.

TABLE 1—THE INFLUENCE OF LOWER FREQUENCY (OUTPUT AT POWER 1 mW) OF LASER ON ALCOHOLIC FERMENTATION

Laser dose in Seconds	Yield of alcohol in ml/100 ml	Percentage of alcohol Increase/decrease (+) (−)
Control	16.5	
1	16.7	+ 1.2
5	19.2	+16.3
10	19.5	+18.7
20	21.2	+28.4
40	21.2	+28.4
80	20.0	+21.2
100	19.0	+15.1
120	16.7	+ 1.2
140	18.0	+ 9.7
180	22.6	+36.9
240	22.0	+33.3
360	21.2	+28.4
480	18.9	+14.5
600	15.3	− 7.2
900	10.9	−33.9
1800	8.8	−46.6

TABLE 2—THE INFLUENCE OF HIGHER FREQUENCY (OUTPUT AT POWER 35 mW) OF LASER ON ALCOHOLIC FERMENTATION

Laser dose in Seconds	Yield of alcohol in ml/100 ml	Percentage of Alcohol Increase/decrease (+)	(−)
Control	23.6		
1	34.6	+46.6	
5	36.6	+55.0	
10	46.6	+97.4	
20	40.0	+69.4	
40	24.6	+ 4.2	
80	21.2		−10.1
100	18.6		−21.1
120	18.6		−21.1
140	13.6		−42.3
180	10.6		−55.0
240	8.4		−64.4
360	7.8		−66.9
480	7.2		−69.4
600	7.2		−69.4
900	5.2		−77.9
1800	4.4		−81.3

It was thus concluded that higher frequency of laser was found to be more effective causing an increase in the yield of alcohol by 97.4%, while lower frequency could enhance the yield only up to 36.9%.

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Letter to the Editor

On the Reported Separation of Conformational Isomers of Cyclohexane Derivatives

Sir,

Recently, Saharia *et al*[1,2] have claimed to have separated the conformers of 4-methyl(III) and 3-methyl-cyclohexane-1, 1-dicarboxylic acids both by degradative (from I and II) and by synthetic (from diethyl malonate) experiments (in the last case, by fractional crystallisation). Such claims, although erroneously made in the past,[3,4] are regarded at present as well-nigh impossible under ordinary



(I) (II) (III)

conditions. We hesitated long to contradict such an obviously absurd proposition particularly because its validity had once been questioned by Price *et al*[5]. Our correspondence with the authors, however, proved futile who preferred to stick to their view and continued to commit the same error in new publications[2,6]. One of our groups (D. N.) repeated the degradative experiments with the two diastereoisomeric acids (I) and (II) following the procedure of the previous authors. The results agreed fairly closely with those of Saharia *et al*[1] except for the fact that the malonic acids derived from both I and II turned out to be identical (mixed m. p. and superimposable IR and NMR spectra) having the expected structure (III), m.p. 175-176° (decomp) (reported[1] m.p.s for the conformers, 176° and 171°). We thus conclude that the alleged claim for separation of conformers is completely baseless and the two isolated acids are, in fact, the same with perhaps slightly different degree of purity. The IR spectra published by Saharia *et al*[1] for their two conformers appear to be identical in the finger print region within instrumental errors.

A full paper[7] with additional information such as assignment of configuration to the two isomeric acids (I) and (II) by ^{1}H and ^{13}C nuclear magnetic resonance (which has turned out to be opposite to that adopted by the previous authors), stereochemistry of the formation of the two acids by Michael addition, and some relevant facts and figures will shortly be published.

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Kinetics of Oxidation of some Phenols by Iron(III)-1,10-Phenanthroline Complex

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Kinetics of oxidation of phenol, *m*-cresol, *p*-cresol, *p*-bromophenol, *p*-chlorophenol have been investigated spectrophotometrically at 35°. The reaction obeys first order kinetics in iron(III); plots of $1/k_1$ versus $1/[1,10\text{-Phenanthroline}]^2$ and $1/k_1$ versus 1/[Substrate] and $1/k_1$ versus $[HSO_4^-]^2$ are straight lines with positive intercepts on the $1/k_1$ axis in each case. The kinetic evidence is in favour of the formation of a mixed ligand complex of iron(III) with 1,10-Phenanthroline and phenol. The reaction gave a good Hammett plot with a ρ^+ value of -1.6.

THE greater oxidising capacity of iron(III) salts in the presence of 1,10-phenanthroline has been reported earlier by Subba Rao *et al*[1]. While extending this kinetic study to oxidation of other classes of organic compounds, the present authors have found that 1,10-phenanthroline catalyses the oxidation of phenol and substituted phenols by iron(III); iron(II) formed is immediately complexed with excess of 1,10-phenanthroline present forming ferroin. In the absence of this ligand the reaction is extremely slow. Some novel kinetic features of this catalysed reaction are reported in this paper. The kinetic pattern of this catalysed reaction is different from that observed in the oxidation of phenols by ferricyanide[2] and mercury(II)[3], detailed kinetic studies of which were already reported.

Experimental

All the materials employed in this kinetic investigation were of analytical reagent grade. The phenols have been redistilled or recrystallised before use. The phenols studied were phenol, *m*-cresol, *p*-cresol, *p*-bromophenol and *p*-chlorophenol. The phenols were standardised bromometrically.

All the kinetic experiments have been carried out keeping the concentration of 1,10-phenanthroline very high in comparison with that of iron(III), so that 1,10-phenanthroline removed through the formation of ferroin (one of the products of the reaction) is negligible, thereby preventing complications due to possible auto-inhibition. To avoid any effects of light, the reaction vessel was coated with the black paint. The course of the reaction has been followed by measuring the optical density of the product ferroin at 510 nm. At this wave length, all the other materials concerned have negligible absorption. The Beer's Law is obeyed under the experimental conditions employed. Control experiments have shown that ferroin is quite stable

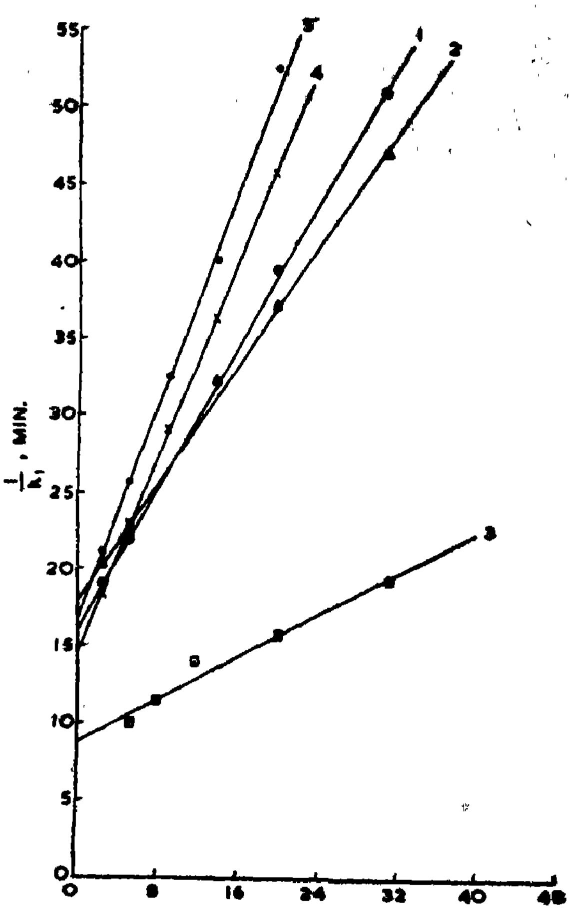


Fig. 1 Plots of $1/k_1$ versus $1/[\text{phen}]^2$
$[Fe(III)] = 8.0 \times 10^{-5}$ M, $[H^+] = 1.3 \times 10^{-2}$ M.
Temp. = 35°
Substrate = 1. Phenol, 2. *m*-cresol; 3. *p*-cresol
Concentration: 4.97×10^{-2} M, 7.41×10^{-3} M, 5.0×10^{-3} M
Substrate: 4. *p*-Chlorophenol, 5. *p*-Bromophenol
Concentration: 1.91×10^{-2} M 2.0×10^{-2}.

under these conditions. Dienone was found to be the product of oxidation as evidenced by the spot test[4] and I.R. studies.

Results and Discussion

All the kinetic runs were carried out under the conditions [phen]* > > [Fe(III)] and [Substrate] > > [Fe(III)]. Under these conditions a plot of log ($D\alpha - D_t$)(where $D\alpha$ and D_t are the optical density values at infinite time and at time t, respectively) versus time is a straight line upto at least 50% of the reaction showing that the reaction is first order with respect to iron(III). The pseudo-first order rate constant, k_1, was calculated from the slope of the straight line.

The values of k_1 were determined at different concentrations of 1, 10-phenanthroline, keeping the concentrations of substrate, iron(III) and H^+ constant. The plots of $1/k_1$ versus $1/[Phen]^2$ were straight lines with positive intercepts on the $1/k_1$ axis (Fig. 1). The values of k_1 were also determined at different concentrations of substrate keeping the concentrations of other materials constant. The plots of $1/k_1$ versus 1/[Substrate] were also straight lines with positive intercepts on the $1/k_1$ axis (Fig. 2).

mixed ligand type, which slowly decomposes to give the products. Earlier studies were made on the iron(III)-phenol complexes by various authors[5].

The effect of sulphate ions on the reaction was studied by varying $[HSO_4^-]$, while keeping the concentrations of other materials constant. The ionic strength was maintained constant with sodium nitrate, although it was found that the effect of the ionic strength on the rate is very small. The rate was found to decrease with increase in the sulphate ion concentration and the quantitative relationship between the rate and the sulphate ion concentration is shown by the linear plot of $1/k_1$ versus $[HSO_4^-]^2$ (since $[SO_4^=] \propto [HSO_4^-]$ at constant $[H^+]$ with positive slope and intercept (Fig. 3). The reaction was found to be inhibited by the increasing concentrations of hydrogen ion.

The studies of Whiteker and Davidson[6] on the sulphate complexes of iron (III) show that, when $[SO_4^=] > 0.01$ *M*, the complex mainly exists as 1 : 2 form. In the presence of excess of 1,10-phenanthroline, the formation of a 1 : 2 complex of iron(III) with the ligand has been reported by Gaines (Jr.), Hammett and Walden[7]. In the presence of sulphate ions, the equilibrium may be represented by

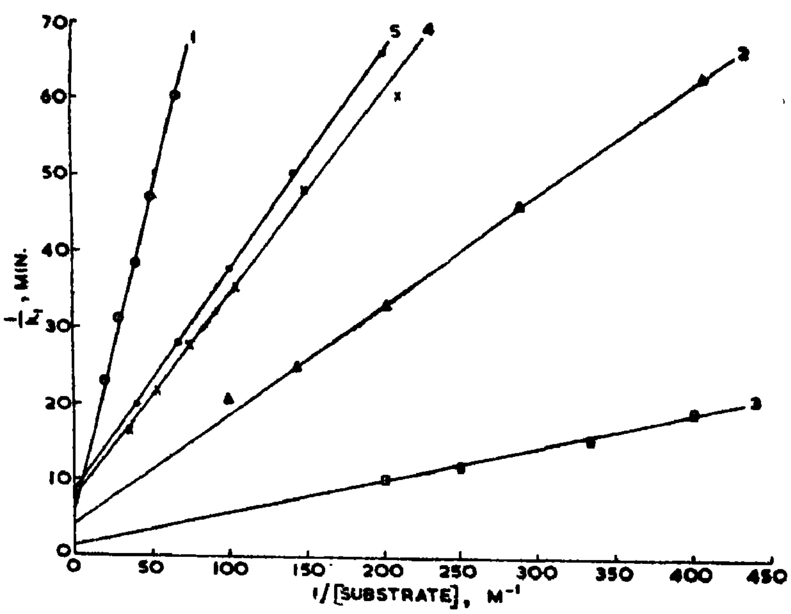


Fig. 2. Plots of $1/k_1$ versus 1/[Substrate]
$[Fe(III)] = 8.0 \times 10^{-5}$ M ; $[H^+] = 1.3 \times 10^{-2}$ M ;
$[Phen] = 4.5 \times 10^{-3}$ M.
Temp. = 35°
1. Phenol ; 2. *m*-cresol, 3. *p*-cresol ;
4. *p*-chlorophenol ; 5 *p*-Bromophenol

Such plots are generally indicative of intermediate complex formation and obtainment of both these plots in the same reaction can be explained by assuming the formation of an intermediate complex of

$$Fe(SO_4)_2^- + 2Phen \rightleftharpoons [Fe(Phen)_2]^{3+} + 2SO_4^=$$

This complex of iron (III) and phenathroline was shown to be different from ferriin by Harris and

*Phen is the abbrevation used for 1,10-phenanthroine.

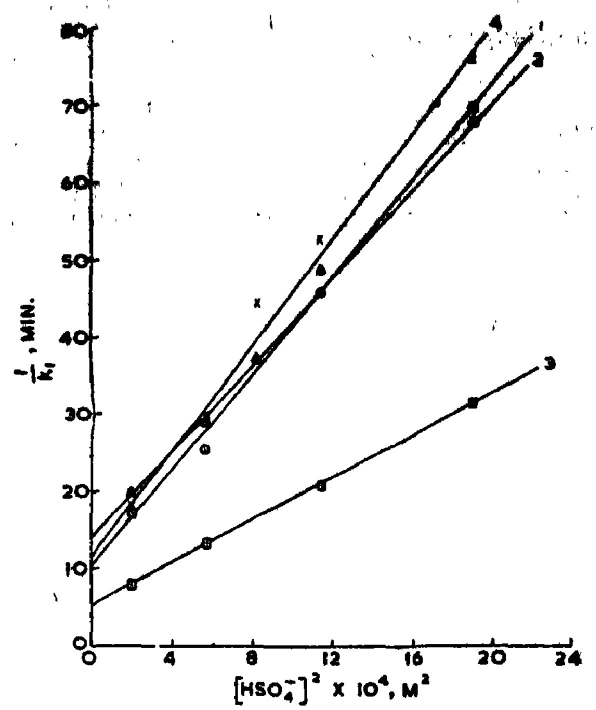


Fig. 3 Plots of $1/k_1$ versus $[HSO^-_4]^2$
$[Fe(III)] = 8.0 \times 10^{-5}$ M ; $[Phen] = 4.5 \times 10^{-3}$ M ;
$[H^+] = 1.3 \times 10^{-2}$ M ; Temp. 35°
Substrate : 1 Phenol, 2.*m*-cresol, 3.*p*-cresol ; 4. *p*-Chlorophenol
Concentation 4.97×10^{-2} M, 7.35×10^{-3} M, 5×10^{-3} M, 1.91×10^{-2} M.

Lockyer[8] from the magnetic studies. Ferriin cannot be obtained by direct mixing of iron (III) and 1,10-phenanthroline, but only by the oxidation of ferroin. The authors propose the following mechanism to account for their kinetic results.

$$Fe(SO_4)_2^- + 2Phen \overset{K_1}{\rightleftharpoons} [Fe(Phen)_2]^{3+} + 2SO_4^-$$

$$[Fe(Phen)_2]^{3+} + Substrate \overset{K_2}{\rightleftharpoons} \underset{(X)}{[Fe(Phen)_2(Sub)]^{3+}}$$

$$X \overset{k}{\longrightarrow} Products.$$

In the mechanism the authors, on the basis of their kinetic observations, assume the formation of a mixed ligand complex involving iron(III), 1,10-phenathroline and the substrate, in which the electron transter occurs ; the electron transfer is facilitated by the presence of 1,10-phenanthroline.

The catalysis by 1,10-phenanthroline may be due to a more favourable electron transfer due to its π-electron system. Further this ligand is also known to stabilise the lower valence state more than the higher one. Thus the reaction between $[Co(en)_2(Phen)]^{3+}$ and Cr^{2+} has been reported to be much faster[9] than that between $[Co(en)_3]^{3+}$ and Cr^{2+}.

It is interesting to note that the kinetic pattern observed in the present reaction is different from that in the case of ferricyanide or mercury (II) oxidation of phenols (*loc. cit*). In the latter cases, the mechanisms involve no intermediate complex formation between the oxidant and the substrate, whereas this has been actually observed in the iron(III) oxidation of phenols in the presence of 1,10-phenanthroline, as supported by the kinetic results.

Rate Law :

The above mechanism proposed by the authors leads to the rate-law,

$$-\frac{d[Fe(III)]}{dt} = \frac{kK_1K_2[Fe(III)][Phen]^2[Substrate]}{K_1K_2[Phen]^2[Substrate]+K_1[Phen]^2+[SO_4^-]^2}$$

The pseudo-first order rate constant k_1 is given by

$$k_1 = \frac{kK_1K_2[Phen]^2[Substrate]}{K_1K_2[Phen]^2[Substrate]+K_1[Phen]^2+[SO_4^-]^2}$$

Taking the reciprocals, we get

$$\frac{1}{k_1} = \frac{1}{k} + \frac{1}{kK_2[Substrate]} + \frac{[SO_4^-]^2}{kK_1K_2[Phen]^2[Substrate]}$$

It is evident from the rate-law that plots of $1/k_1$ versus 1/[Substrate], $1/k_1$ versus $1/[Phen]^2$ and $1/k_1$ versus $[SO_4^-]^2$ or $[HSO_4^-]^2$ at constant $[H^+]$, should be straight lines, which were, however, actually observed. This supports the given mechanism.

The values of k, K_1 and K_2 can be calculated from the values of slopes and intercepts of the plots of $1/k_1$ versus 1/[Substrate] and $1/k_1$ versus $1/[Phen]^2$. A value of 0.075 was used for the second ionization constant of sulphuric acid as reported by Doyle and Davidson[10]. The values of the above constants at 35° were presented in Table 1. It is evident that the values of K_1 calculated from the data of oxidation of various phenols are in the same order and reasonably good agreement.

TABLE —1 VALUES OF k, K_1 K_2, AT, 35° FOR THE OXIDATION OF VARIOUS PHENOLS

Substrate	k min^{-1}	K_1*	K_2 litre. $mole^{-1}$
Phenol	0.18	12.30	10.06
p-Cresol	0.63	12.10	46.77
m-Cresol	0.25	17.20	38.57
p-Chlorophenol	0.13	6.20	52.25
p-Bromophenol	0.12	7.30	50.00

*The value reported is the mean of the two values that can be calculated from the slope and intercepts of the plots in Figures 1 and 2.

The authors found that a Hammett plot of log k versus σ^+ was a straight line (Fig.4), which yielded

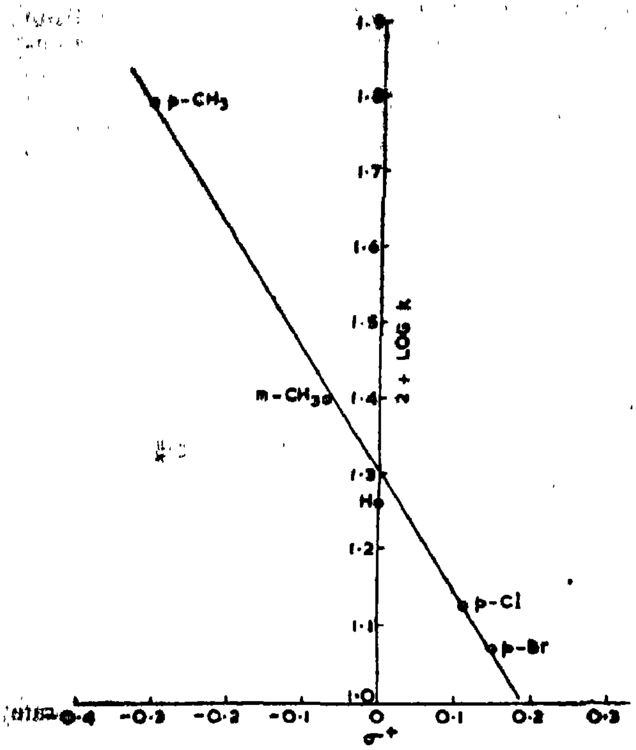


Fig. 4 Plot of (2 + log k) versus σ^+

a ρ^+ value of -1.6. The negative value of ρ^+ shows that the reaction proceeds through a cationic centre. The values of σ^+ used were those of Okamoto and Brown[11].

Acknowledgement

Three of the authors (B.A.N.M., K.S.M and R.V.S.M.) thank the University Grants Commission and the Council of Scientific and Industrial Research, India for the award of Junior Research Fellowships.

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Kinetics and Mechanisms of the Acid-Catalyzed Dissociation of *Trans*-Dicyano*bis*biguanidecobalt(III) Chloride

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Investigations were carried out on the acid-catalyzed dissociation of *trans*-dicyano*bis*biguanidecobalt(III) ion in presence of 0.1-0.5M perchloric acid in the temperature range 28°- 40°. In this range, only one 'biguanide' dissociates from the complex ion with the formation of (*cis*) diaquo*trans*dicyano*mono*biguanidecobalt(III) ion. Activation parameters were evaluated in the usual way ($\triangle H^{\ddagger} = 15.6$ kcals mol^{-1} ; $\triangle S^{\ddagger} = -24$ e.u.) and these values indicate that the mechanism of dissociation is similar to other cobalt-biguanide complexes. Bond-breaking in the transtition state is more important than other factors.

NUMEROUS studies on the kinetics of th edissociation of bidentate chelates from cobalt(III) complexes are available in literature[1-5]. Protonation mechanism has been suggested for the acid-catalyzed dissociation of these flexible bidentate basic ligands[6]. In presence of acidic aqueous solution, biguanide complexes of cobalt(III), form protonated intermediates (conjugate acids)[1]. The presence of a non-labile inert ligand may have an influence on the formation of the conjugate acid and thus on the rate. In order to study the effect of such ligands, present work was undertaken to investigate the influence of cyanide on the dissociation of the biguanide in *trans*-dicyano*bis*biguanidecobalt(III) ion. In acid solution, this complex ion release biguanides in stages, the conditions being wide apart in acidity and temperature and in present investigation only the first step of dissociation with the formation of *trans*-dicyano (*cis*) diaquo*mono*biguanidecobalt(III) ion is reported. Along with this complex ion, an attempt was made to study the dissociation of the similar complex ion *trans*-dicyano*bis*ethylenediaminecobalt(III) ion and all these are reported in the following pages.

Experimental

Reagents :

Trans-Dicyano-*bis*-biguanidecobalt(III) chloride was prepared of the method of Sengupta and Ray[7]. It was recrystallized from the aqueous solution and was used for kinetic studies. Found : Co-17. 32 ; N-47.96 percent. Calculated for $[Co(C_2N_5H_7)_2(CN)_2]$ Cl : Co-17.00 ; N-48.29 percent.

Trans-Dicyano-*bis*-ethylenediaminecobalt(III) chloride. The corresponding sulphate was prepared by the method of Ray and Sharma[8] and its purity was checked by analysis Found : N-26.95 and Co-9.41 ; Calculated for $[Co(C_2H_8N_2)_2(CN)_2]_2\ SO_4.\ 3H_2O$ and N-27.45 Co-9.64. The perchlorate salt was prepared in solution before use by the metathesis of an equivalent amount of complex sulphate with barium perchlorate in solution. Stock solutions of perchloric acid were prepared using reagent grade (G.R.E Merck) acid and were standardized as usual.

Sodium perchlorate (fluka) was twice recrystallized from water and dried at 150° before use.

All other chemicals used were of reagent grade or else were purified by suitable methods. Distilled water redistilled with a little amount of alkali and potassium permanganate in an all glass still was used for making the solutions.

Apparatus and procedure : A Beckman DU-2 spectrophotometer was used for absorbance measurements. Spectra of the solutions of 5×10^{-4}M complex ion with different acid concentrations from 0.01 -2*M* perchloric acid were recorded immediately after preparation and also after 1, 2, 3 hours ; 1, 2, etc. upto 10 days keeping the solutions at room temperature. There was an initial change in the absorption spectra of all the solutions. The absorption spectra in the acid range 0 05-2.0 *M* for the biguanide complex remains almost unchanged after 2-3 days. At this stage only one 'biguanide' dissociates from the experimental complex with the formation of $[Co\ (BigH)(H_2O)_2(CN)_2]^+$ and represents the absorbance for diaquo complex which was actually isolated from the solution. Figure 1 records the spectra of 0.0005 *M* aqueous solution of the experimental, and the product diaquodicyano-*mono*-biguanidecobalt(III), complex ions. At 80°, spectra of the siolutions

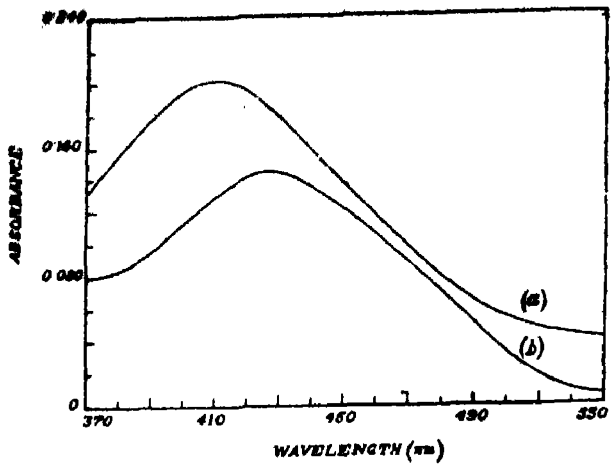


Fig. 1. Absorption spectra of 0.0005 M aqueous solutions of (*a*) *trans*-dicyanobisbiguanidecobalt(III) ion and (*b*) *trans*-dicyano*cis*-diaquo*mono*biguanidecobalt(III) ion (absorbance cm^{-1}).

containing 3-5 M perchloric acid change rapidly and after 1 day become identical with that of Co^{2+} ion, which may form by the stepwise dissociation of both 'biguanide' chelates and ultimate decomposition of the resulting tetraaquo complex. In the present investigation only the dissociation of the first chelate is reported. Kinetic runs were carried out in stoppered Jena volumetric flasks placed in a thermostat where the temperature was held to within ± 0.1° of the desired value. At suitable intervals, 2 ml portions of the solutions were withdrawn and quenched by putting in a pyrex glass test tube placed in ice and absorbance measurements were made in one cm stoppered quartz cells after raising the temperature to room temperature. The rate of aquation of the complex in acid medium was measured in an excess of the reagent such that the first order rate law was applicable. Ionic strength was maintained with required amount of sodium perchlorate. Measurements were carried out at 410 nm, where the difference between the absorption of the complex and its reaction products is maximum. The pseudo first order rate constants were evaluated graphically by plotting $\log(A_0-A_\infty)/(A_t-A_\infty)$ against 'time' where A_0, A_t and A_∞ represent, absorbance at start, time '*t*' and at the end of the reaction respectively.

Indentification of the dissociation products :

500 ml of a 0.005 M solution of the complex in 0.2 M perchloric acid was kept at room temperature for 48 hours. It was then dried up completely in a rotary evaporator and taken with *ca.* 20 ml of water and allowed to crystallize in air. Small orange-yellow crystals of $[Co(C_2N_5H_7)(H_2O)_2(CN)_2]ClO_4$ appeared in 3-4 days along with white prismatic crystals of biguanide perchlorate. These orange-yellow crystals were separated by hand picking and recrystallized from water and analysed. Cobaltous ion could not be detected from the solution at this stage by spectrophotometric method[9].

Instead of perchloric acid, when nitric acid was used in the dissociation study, better yield of the rhombic ruby red crystals of $[Co(C_2H_7N_5)(H_2O)_2(CN)_2]NO_3$ were obtained along with biguanide nitrate.

Analysis : Orange-yellow compound : found-Co. 17.30 ; N. 27.90 ; Cl. 10.43 ; H_2O-10.21 $[Co(C_2H_7N_5)(H_2O)_2(CN)_2]ClO_4$ requires-Co. 16.95 ; N. 28.20 ; Cl. 10.20 ; H_2O-10.34 Ruby-red compound : found-Co. 19.42 ; N. 36.47 ; H_2O-10.30 $[Co(C_2H_7N_5)(H_2O)_2(CN)_2]NO_3$ requires-Co. 19.04 ; N. 36.12 ; H_2O-11.61

Thermogravimetry of the product compounds showed that these compounds did not loose any significant amount of their weight before 180° indicating 'H_2O' must have been coordinated to metal atom. When the dissociation reaction was carried out at 90° in 3*M* $HClO_4$, within few hours the solution looses its colour with complete dissociation of the complex. The solution was evaporated in a rotary evaporator and Co^{2+} ion and 'biguanide perchlorate' were identified by spectrophotometric method[9] and copper-biguanide complex formation[10]. Cyanide, as HCN, was identified by blowing air successively through the experimental solution and small amount of dil. sodium hydroxide solution throughout the experimental run, and then identifying CN^- in this NaOH solution by the usual procedure.

Results and Discussion

The values of the pseudo first order rate constants for the dissociation of the complex at 28° and μ=0.5 but different concentrations of perchloic acid are given in Table 1. The observed rate of dissociation is same for different amounts of complex ion, so the rate is first order dependent on complex concentration. A plot of k_{obs} vs $[H^+]$ (Fig. 2) gives a straight line passing through origin indicating that the rate is also first order with respect to H^+ ion.

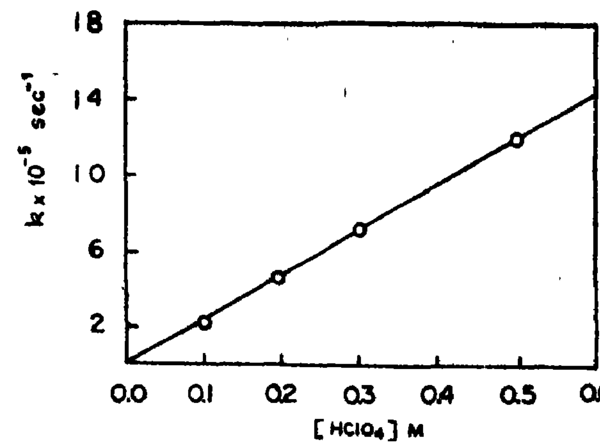


Fig. 2. Effect of acid ($HClO_4$) concentration on the rate of dissociation at a particular temperature (28°) μ, 0.5.

TABLE—1 EFFECT OF ACID CONCENTRATION ON THE DISSOCIATION OF *trans*-DICYANO*bis*BIGUANIDECOBALT(III) ION. $\mu = 0.5$; TEMP. 28°.

Complex $\times 10^{-3}$M	0.5	1.0	0.5	0.5	0.5
$HClO_4$, M	0.1	0.2	0.2	0.3	0.5
$10^5 k$ sec^{-1}	2.19	4.50	4.68	7.18	12.0

The dissociation of the complex in acid medium may be represented by the overall equation of the following type.

$$Co(BH)_2(CN)_2^+ + H^+ + 2H_2O \longrightarrow Co(BH)(H_2O)_2(CN)_2^+ + BH_2^+ \quad \ldots (1)$$

where 'BH' stands for a molecule of biguanide. This reaction occurs through the formation of a protonated intermediate as in the case of other biguanide complexes[1], where the rate of dissociation runs parallel to the basicity of the ligand.

$$Co(BH)_2(CN)_2^+ + H^+ \overset{\text{Instantaneous}}{\rightleftharpoons} Co(BH)(BH_2)(CN)_2^{2+}$$

$$\xrightarrow[+2H_2O]{\text{Slow}} Co(BH)(H_2O)_2(CN)_2^+ + BH_2^+ \quad \ldots (2)$$

Dissociation of the *trans*-dicyano*bis*ethylenediamine complex ion in presence of 1-5 M perchloric acid at room temperature and also at 90° was investigated. In this case, as 'en' (=ethylenediamine) do not have any centre for protonation[1], no protonated intermediate formation takes place which can initiate an acid-catalyzed dissociation. Consequently the reaction rate is extremely slow, and the complex is perfectly inert in this condition. No observable change was noticed in the course of seven days.

The effect of ionic strength on the rate of dissociation of complex ion is given in Table 2. Rate increases with ionic concentration. No account could be made for this observation. Activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were evaluated by making use of Eyring[11] equation of the form

TABLE—2 EFFECT OF IONIC STRENGTH ON THE DISSOCIATION OF *trans*-DICYANO*bis*BIGUANIDECOBALT(III) CHLORIDE

Complex	5×10^{-4}M		$HClO_4$-0.2 M	Temp. 28°
'μ'M	0.2	0.3	0.4	0.5
10^5K sec^{-1}	2.43	2.63	3.37	4.68

$$\log \frac{kh}{kT} = \frac{\Delta S^{\ddagger}}{2.303\,R} - \frac{\Delta H^{\ddagger}}{2.303\,RT} + \log\,[HClO_4].$$

where h, k and R have their usual significance (Fig. 3). The observed values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 15.6 ± 1.2 kcals mol^{-1} and -24 ± 3 e.u.

A comparison of the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values obtained in this case along with the acid-catalyzed dissociation of *tris*-biguanidecobalt(III) ion and diaquo-*bis*-biguanidecobalt(III) ion (Table 3) indicates that similar mechanism operates in all the three cases.

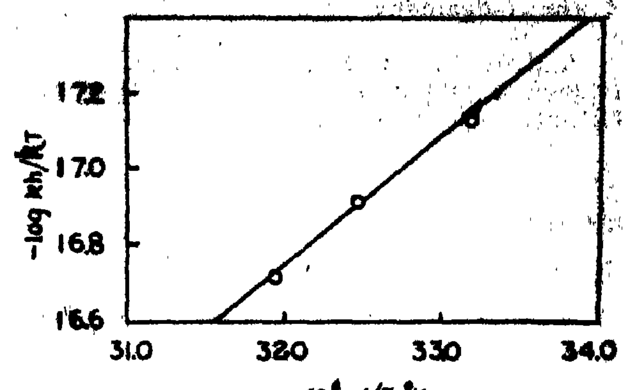


Fig. 3. Eyring plot for the dissociation of *trans*dicyano-*bis*biguanidecobalt(III) ion.

TABLE—3 ACTIVATION PARAMETERS AND RATE OF DISSOCIATION OF SOME COBALT(III)-BIGUANIDE COMPLEXES

Complex	k_{obd}, sec^{-1} $HClO_4$-0.5 M $\mu = 1$M, 40°	$\Delta H^{\ddagger}$ kcal/mol	$\Delta S^{\ddagger}$ e.u.	Ref.
$Co(BigH)_3^{3+}$	1.36×10^{-5} (extrapolated value)	11.1	−31.5	1
cis-$Co(BigH)_2(H_2O)_2^{3+}$	9.5×10^{-6} (extrapolated value)	15.2	−31.6	12
trans-$Co(BigH)_2(CN)_2^+$	6.3×10^{-4}	15.6	−24.0	This work

In this complex, the electron donation by cyanide to the metal atom, is partly taken back through π-bond, leaving the metal atom apparently more positive than in *tris*-biguanide complex. Thus cobalt atom aquires better acceptor properties for electrons and the metal-ligand (biguanide) bonds become stronger. Consequently greater energy ($\Delta H^{\ddagger}$) is required for the rupture of the bond as observed in this case. The $\Delta H^{\ddagger}$ values for this complex and that of $Co(BigH)_2(H_2O)_2^{3+}$ are equal, showing metal-ligand bonds are of equal strength, but the reduced cationic, charge of this complex favours the formation of the intermediate more than that with the diaquo-complex with positively charged proton, and the aquation rate becomes higher. The electron withdrawal by *trans*-cyanide ions, lowers the electron density around cobalt atom equally in all directions and the bond formation by the incoming 'water molecule' is not favoured until and unless the departure of the 'biguanide' takes place. So, "bond breaking" is the only important factor in the transition state.

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Kinetics and Mechanism of Oxidation of Methyl Mandelate by Manganese(III) Pyrophosphate

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Where as a ketoester is the product of oxidation of the ester of an hydroxy acid by chromium(VI) and by vanadium(V), benzaldehyde is the product of oxidation of methyl mandelate by manganese(III) pyrophosphate. Kinetics of the oxidation of the methyl mandelate by manganese(III) pyrophosphate has been studied. The reaction is first order each in ester and in manganese(III) pyrophosphate. The rate is proportional to the square of the concentration of hydrogen ion but it is inversely proportional to the concentration of free pyrophosphate in the solution. Addition of manganese(II) ion has no effect on the rate of reaction. The rate is also affected by the composition of the solvent acetic acid water mixture, the rate decreases in increase in the proportion of acetic acid in the solvent mixture. The kinetic isotope effect kH/kD has a value of 1.90 and shows that C-H is not involved in the rate determining step. The heat of activation and entropy of activation have values of 25.0 k.cals $mole^{-1}$ and 15.0 e.u. respectively. A mechanism which is consistent with the observed rate laws and other experimental facts has been proposed.

OXIDATION of an ester of α-hydroxy carboxylic acid R.CH(OH)COOR′ by chromium(VI)[1,2] and by vanadium(V)[3] gives a ketoester R.COC.OOR′. Thus in these oxidations the esters behave like secondary alcohols. In view of the report[4] that monohydric alcohols are not attack by manganese(III) pyrophosphate, it was anticipated that these esters will be stable towards manganese (III) pyrophosphate. However, preliminary studies showed that methyl mandelate reacted with manganese(III) pyrophosphate and produced benzaldehyde. It was therefore fruitful to examine the kinetics of the oxidation of methyl mandelate with manganese(III) pyrophosphate with a view to elucidate the mechanism of the oxidation.

Experimental

(a) *Material used* :

(i) *Preparation of methyl mandelate* : 50 gms of mandelic acid, 40 gms of methyl alcohol and 1 gm of concentrated sulphuric acid were mixed in a round bottomed flask and the mixture was refluxed for about six hours using double surface condenser. Then excess alcohol was distilled out on a water bath. The residue was shaken with aqueous sodium hydrogen carbonate solution to neutralise the unreacted acid. It was filtered and washed with water, the solid ester was dried and recrystallised from the mixture of benzene and ligroin, m.p. 57°..

(ii) *Preparation of α-deuterated methyl mandelate* : Deuteromandelic acid[5] was prepared by equilibriating sodium mandelate three times in a sealed tube at 150° for seven days with sodium hydroxide (5%) in deuterium oxide (99.8%) labiled hydrogen was then removed by recrystallising the free acid twice from water (m.p. 120-21°). This deuterated mandelic acid was esterified by method described in (i) above. NMR spectra of the sample showed that more than 95% deuteration had been achieved.

(iii) *Preparation of 1-phenyl ethanol* : 1-phenyl ethanol was prepared by the reduction of acetophenone with sodium borohydride and further purified by refluxing over 2:4,-dinitrophenylhydrazine followed by distillation. Manganese(III) pyrophosphate was prepared from manganese(II) sulphate by the method of Lingnane and Karplus[6]. Sodium pyrophosphate (Albert and Willson, England) was used for this purpose. Acetic acid (B.D.H.) was purified by the method described by Eichelberger and LaMer[7]. Other chemicals used were of B.D.H. (Analar) specifications.

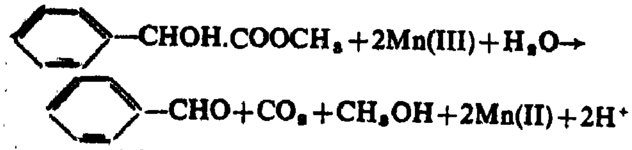
(b) *Kinetic measurements* :

The methyl mandelate is less soluble in water. However this is soluble in 40 percent acetic acid (v/v). Solution of methyl mandelate was therefore, prepared in glacial acetic acid. A known volume of the ester was mixed with predetermined volume of glacial acetic acid, sulfuric acid and of sodium pyrophosphate solution. The manganese(III) pyrophosphate solution was last to be added. The volume of the reaction mixture was always kept 20 ml. The reaction was carried out in glass stoppered flask at constant temperature. Sulphuric

acid was used to maintain pH of the solution. The temperature was maintained constant by use of a thermostat which maintained temperature constant to $\pm 0.02°$. The reacting substances were brought to thermostat temperature before use and then mixed in reaction flask also previously brought to thermostat temperature. Aliquots were withdrawn at known intervals of time and the concentration of manganese(III) left unreacted was estimated iodometrically taking precautions to minimise air oxidation of iodide[8]. The initial rate of reaction were estimated from the plot of the titre values against time. This plot was straight line for about first 10-15 percent of the reaction and included about 5 to 6 measurements. Similar kinetic measurements were carried out for mandelic acid and for 1-phenyl ethanol. Hydrolysis of methyl mandelate under the kinetic conditions was also examined.

(c) *Product studo* :

The product study was made under kinetic conditions. The oxidised mixture was completely neutralised by aqueous sodium bicarbonate and then extracted with ether. The aqueous layer (which would contain benzoyl formic acid if any formed) left after extraction, was made acidic and 2 : 4,-dinitrophenyl hydrazine solution in $2N$ hydrochloric acid was added, no ppt. of 2:4,-dinitrophenyl hydrazone was obtained. This indicates that benzoyl formic acid is not a product of oxidation. The etheral layer was heated on a water bath to remove the ether, cooled, made just acidic and 2:4 dinitrophenyl hydrazine (in $2N$ hydrochloric acid) solution was added. This gave 2:4,-dinitrophenyl hydrazone, recrystallised from alcohol m.p. 235-237° m.m.p., 236-37°. The formation of 2:4,-dinitrophenyl hydrazone suggests that benzaldehyde is the product of oxidation.



The yield of benzaldehyde is 90% of the expected yield estimated as 2:4,-dinitrophenyl hydrazone[9].

Acetophenone was the product of oxidation of 1-phenyl ethanol by manganese(III) pyrophosphate (identified as its 2:4,-dinitrophenyl hydrazone).

(d) *Kinetic Isotope Effect* :

This study was measuring the rates of reactions of methyl mandelate and α-deuteromethyl mandelate at 35°, a value of kH/kD = 1·90 was obtained for the kinetic isotope effect.

Results and Discussion

The initial rates are proportional to the concentration of manganese(III) (Table 1). The rates are also proportional to the concentration of methyl mandelate (Table 2). The reaction is not affected by the addition of manganese(II). The reaction was studied at vorious pH in the pH range 0·30 to 0.75. The rate is proportional to square of the hydrogen ion concentration (Table 4). The reaction is retarded by the addition of pyrophosphate. It is found that the product of rate

TABLE—1 VARIATION OF MANGANESE(III) IN METHYL MANDELATE

Solvent : 40 percent acetic acid. 60 percent water (v/v).
[Ester] = $3.5 \times 10^{-2} M$; [Pyrophosphate] = $5.0 \times 10^{-2} M$
pH = 0.3 ; Temperature = 35°

$[Mn(III)] \times 10^{3}$ moles litre^{-1}	$10^{4} \times$ Initial rate moles of Mn(III) litre^{-1} min^{-1}	$10^{2} \times$ Initial rate [Mn(III)] min^{-1}
3.39	0.573	1.73
5.09	0.892	1.75
6.78	1.290	1.90
6.48	2.020	2.38
10.20	2.460	2.40

TABLE—2 VARIATION OF INITIAL RATE WITH CONCENTRATION OF METHYL-MANDELATE

Solvent : 40 percent acetic acid ; 60 percent water (v/v) :
[Mn(III)] = $3.39 \times 10^{-3} M$; [Pyrophosphate] = $2.5 \times 10^{-2} M$
pH = 0.3 ; Temperature = 35°

[Ester] $\times 10^{2}$ moles litre^{-1}	$10^{4} \times$ initial rate moles of Mn(III) litre^{-1} min^{-1}	$10^{3} \times$ initial rate [Ester] min^{-1}
1.00	0.60	6.00
2.00	1.19	5.95
2.50	1.31	5.24
3.00	1.57	5.23
3.50	1.90	5.43
4.00	2.30	5.75

TABLE—3 EFFECT OF THE CONCENTRATION OF PYROPHOSPHATE IN METHYL MANDELATE

Solvent : 40 percent acetic acid ; 60 percent water (v/v).
[Ester] = $3.5 \times 10^{-2} M$; [Mn(III)] = $3.30 \times 10^{-3} M$
pH = 0.3 ; Temperature = 35°

$10^{2} \times$ [Py] moles litre^{-1}	[Py] $\times 10^{2}$ moles litre^{-1}	$10^{6} \times$ Initial rate moles of Mn(III) litre^{-1} min^{-1}	$10^{4} \times$ Initial rate/$[Py]_{free}$ mole^{2}litre^{-2} min^{-1}
2.50	1.48	1.64	1.42
3.75	2.73	0.93	2.54
5.00	3.98	0.63	2.50

Py = Pyrophosphate

TABLE—4 VARIATION OF pH IN METHYL MANDELATE

Solvent : 40 percent acetie acid ; 60 percent water (v/v).
[Mn(III)] = $3.39 \times 10^{-3} M$; [Pyrophosphate] = $2.5 \times 10^{-2} M$
[Ester] = $3.5 \times 10^{-2} M$; Temperature = 35°

pH	$10^{4} \times$ Initial rate moles of Mn(III) litre^{-1} min^{-1}	[H^{+}] moles litre^{-1}	$10^{4} \times$ Initial rate/$[H^{+}]^{2}$ litre^{-1} mole^{-1} min^{-1}
0.30	1.920	0.501	7.55
0.45	1.090	0.355	8.60
0.60	0.514	0.251	8.13
0.75	0.205	0.178	6.50

TABLE—5 VARIATION OF RATE WITH PERCENTAGE ACETIC ACID IN METHYL MANDELATE

[Ester]=3.5×10^{-3} *M*; [Pyrophosphate]=2.5×10^{-4} *M*
[Mn(III)]=3.39×10^{-3} *M*; *p*H=0.3: Temperature=35°

Percentage acetic acid (v/v)	$10^4 \times$ Initial rate moles of Mn(III) litre^{-1} min^{-1}
30	2.23
40	1.91
50	1.49
60	1.17

and the free pyrophosphate concentration is constant. The reaction is dependent on the solvent composition. The rate decreases with increase in the proportion of acetic acid in the solvent mixture. A plot of initial rate against percentage of the acetic acid in the solvent mixture is straight line with negative slope (Fig. 1). The reaction was studied at different temperature in the range 30° to 45° (cf. Table 6). A plot of log (initial rate) against inverse

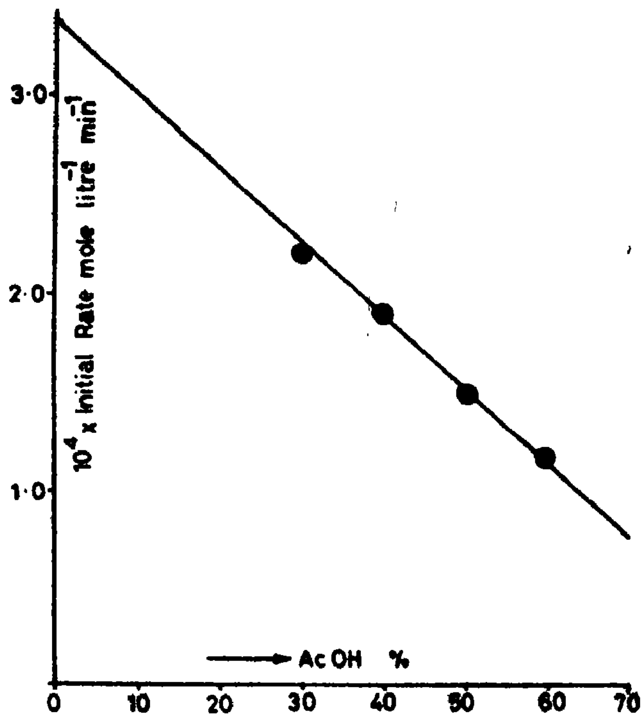


Fig. 1. Effect of percentage Acetic acid on initial rate oxidation of methyl mandelate by manganese(III) pyrophosphate.

TABLE—6 EFFECT OF TEMPERATURE ON THE RATE OF OXIDATION

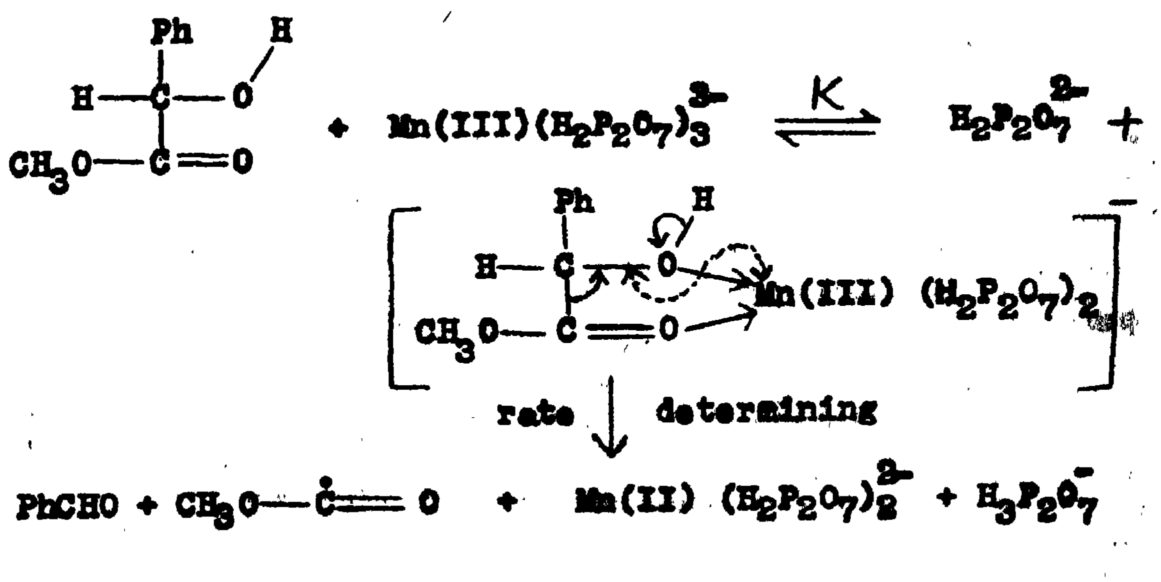
Solvent: 40 percent acetic acid; 60 percent water (v/v).
[Mn(III)]=3.39×10^{-3} *M*; [Pyrophosphate]=2.5×10^{-3} *M*
[Ester]=3.5×10^{-3} *M*; *p*H=0.3

Temperature °k	$10^4 \times$ Initial rate mole of Mn(III) litre^{-1} min^{-1}	
303	1.004	$\Delta H^{\ddagger}=25.0$
308	1.920	k.cal. mole^{-1}
313	3.460	$\Delta S^{\ddagger}=+15.0$ e.u.
318	7.280	

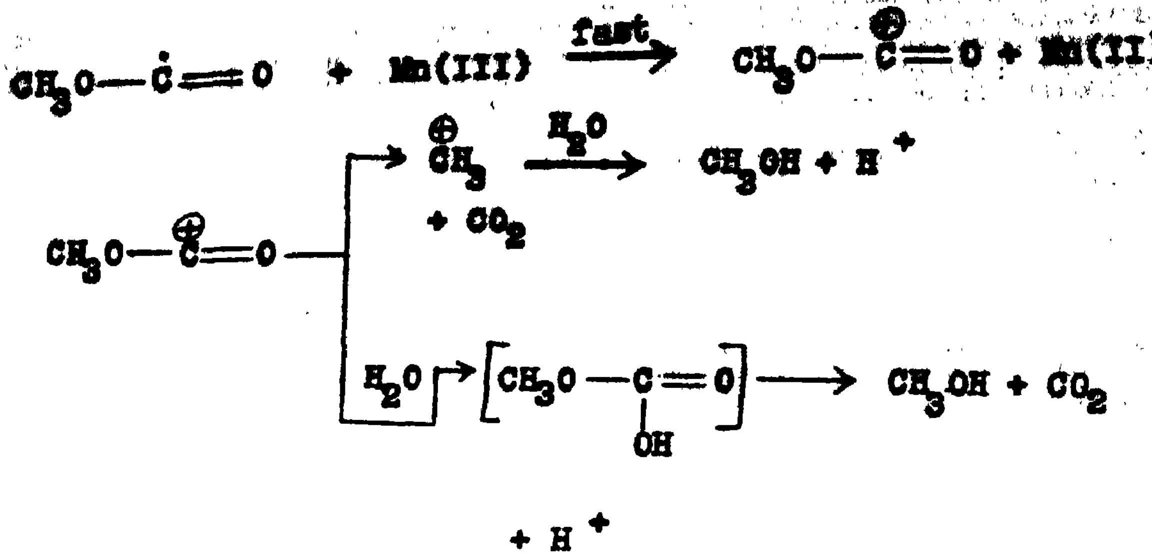
of absolute temperature gives a straight line. Thus Arrhineous equation is valid. Heat of activation and entropy of activation for the reaction estimated from the data in Table 6 have values of 25.0 k.cals. mole^{-1} and +15.0 e.u. respectively.

The value of kH/kD for methyl mandelate is found to be 1.90 at (35°). This can not be primary kinetic isotope effect since the C-H bond fission would lead to the formation of ketoester. It is therefore, appears that the kinetic isotope effect observed in the present case is a secondary kinetic isotope effect which is known to have a values of 1-2[8].

A study of the hydrolysis of methyl mandelate under the experimental condition, shows that the methyl mandelate is not appreciably hydrolysed under the conditions used for kinetic studies. Further the rate of oxidation of 1-phenyl ethanol, methyl mandelate and mandelic acid follows the order mandelic-acid>methyl mandelate>1-phenyl ethanol. These results find a satisfactory explanation on the basis of following mechanism.



(1)



(2)

(3)

The compound HO—C(=O)—OCH_3 is unstable[10] and would immediately break into CO_2 and CH_3OH.

On this basis the initial rate would be given by

$$\text{Initial rate} = -\frac{d[Mn(III)]}{dt} = \frac{k[\text{Ester}][Mn(III)]}{\frac{[H_2P_2O_7^{2-}]}{K}+[\text{Ester}]}$$

The value of $\frac{[H_2P_2O_7^{2-}]}{K}$ was estimated from the effect of pyrophosphate concentration on the initial rate. At $pH=0.3$ and temperature of 35° the value of $\frac{[H_2P_2O_7^{2-}]}{K}$ for the reaction of methyl mandelate is 0.200. This value is much in excess over the highest concentration of the methyl mandelate used in kinetic studies (i.e. 0.04 mole $litre^{-1}$). Hence the initial rate equation takes the form.

$$-\frac{d[Mn(III)]}{dt} = \frac{k.K[\text{Ester}][Mn(III)]}{[H_2P_2O_7^{2-}]}$$

$$= \frac{K'[\text{Ester}][Mn(III)]}{[H_2P_2O_7^{2-}]}$$

(where $K'=k.K$)

This accords with the experimental results. This implies that the value of K, the equilibrium constant for the complex formation is very small. This is no surprising since $H_2P_2O_7^{2-}$ coordinates strongly with manganese (III). The effect of the solvent composition can be explained if it is assumed that the following equilibrium exist.

$$CH_3COOH + Mn(H_2P_2O_7)_3^{3-} \overset{K'}{\rightleftharpoons} [Mn(H_2P_2O_7)_2(CH_3COO)]^{2-} + H_2P_2O_7^{-}$$

The value of the equilibrium constant K' is expected to be small because pyrophosphate anions coordinate extremely strongly with manganese(III). However, because the large concentration of acetic acid, the equilibrium would be shifted to the right to an appreciable extent. If it is now assumed that $[Mn(H_2P_2O_7)_2.\ (CH_3COO)]^{2-}$ is a much poorer oxidant compare to $Mn(H_2P_2O_7)_3^{3-}$ the rate would be given by

$$\text{Rate} = k'[Mn(III)]\left\{1-\frac{K''[HAC]}{[H_2P_2O_7^{-}]_{free}}\right\}$$

as observed.

Watters and Kolthoff[11] have shown that although manganese (III) complex is shown by the formula $Mn(III)-(H_2P_2O_7)_3^{3-}$, the formula of the complex can be $Mn(III)(H_2P_2O_7)_3^{3-}$ to $Mn(III)(H_2P_2O_7)_3$, depending on the pH of the solution. The equation (1) is but one representative of the whole series of equilibria involving free and complexed pyrophosphate anions $H_2P_2O_7^{2-}$, $H_3P_2O_7^{-}$ etc., each of which is a weak acid. Watters and Kolthoff[11] have shown that both the structure and redox-potential of manganese (III)—pyrophosphate are pH dependent. Again shifts in equilibria between $H_3P_2O_7^{-}$ and $H_2P_2O_7^{2-}$ groups will undoubtedly change the case with which the ester molecule can displace of pyrophosphate group in forming the complex. Since the ligand (pyrophosphate) can undergo ionisation both before and after being bound to Mn(III), dependence of the rates of oxidations over a wider pH range is complex and rather uninformative. However, in the range of acidity examined here, the variations in the extent of association of hydrogen ions with pyrophospheric acid can be represented as (Watters and Kolthoff[1].

$$Mn(III)(H_2P_2O_7)_3^{3-} + 2H^+ \rightleftharpoons Mn(III)(H_2P_2O_7)_2(H_3P_2O_7)$$

The rate dependence on hydrogen ions, in the range of acidity examined, therefore, suggests that the active species in these oxidations is $Mn(III)(H_2P_2O_7)_2(H_2P_2O_7)^{-}$.

That the rate of oxidation of methyl mandelate is

much greater than that of 1-phenyl ethanol but is less than that of mandelic acid, suggests the importance of chelate complex formation in these oxidations. That chelate formation may result in the increased rate of oxidation, has also been observed in the case of oxidation of ketones and hydroxy ketones by vanadium(V). Thus with vanadium (V), the hydroxy ketone is oxidised about 200 times much rapidly[12]. It has been observed (Duke[13]) that chelation of the type postulated in equation (1) leads to a lowering of the activation energy for the C-C fission process by some 25-30 k.cals. mole^{-1} and facilitates C-C fission. The reactivity of methyl mandelate relative to that of 1-phenyl ethanol (secondary alcohol), may, therefore, be treated to the ability of methyl mandelate to form chelate complex with manganese(III) pyrophosphate.

It is instructive to compare the behaviour of manganese(III) pyrophosphate in these oxidations with those of chromium(VI) and vanadium(V). Oxidation of methyl-mandelate with chromium (VI) and with vanadium(V) gives the corresponding ketoester by C-H fission in the rate determining step (Jain [14]; Sharma[15]). By contrast the oxidation of methyl mandelate by manganese(III) pyrophosphate gives benzaldehyde by C-C fission in the rate determining step. Bakore and Narain[16] have shown that a distinction can be made between systems involving C-H fission and those involving C-C fission in the oxidation of α-hydroxy acids by chromium (VI) on the basis of over all entropy of activation also (cf. McAuley[17]). The thermodynamic parameters reported in Table 7 are consistent with these views. Thus whereas chromium(VI) and vanadium(V) function as two electron oxidant for the methyl-mandelate ; manganese(III) pyrophosphate functions as one electron oxidant. Thus oxidation of the methyl mandelate can be used to distinguish between one electron and two electron oxidants.

TABLE—7 THERMODYNAMIC PARAMETERS FOR OXIDATION OF METHYL MANDELATE.

Oxidant	$\Delta H^{\ddagger}$ k.cal.mole^{-1}	$\Delta S^{\ddagger}$ e.u.	Ref
Chromium (VI)	12.6	−26.3	(14)
Vanadium(V)	11.4	−25.5	(15)
Manganese(III)-pyrophosphate.	25.0	+15.0	present work

Acknowledgement

We thank Prof. B. Venkataraman and Dr. G. Govil (T.I.F.R., Bombay) for the n.m.r. spectra of the deutrated sample.

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Thermodynamic Parameters of Pr(III), Nd(III) and Sm(III) Chelates with Glutamic Acid

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The thermodynamic parameters of Pr(III), Nd(III) and Sm(III) chelates with glutamic acid were determined potentiometrically in aqueous solution at 30±0.1° and 40±0.1° in an ionic strength of 0.1 M KCl. The stability constant (log k), change in free energy (△G), enthalpy (△H) and entropy (△S) for the complexes are reported. The increase in the values of stability constants of rare-earth metal ions with increase in atomic number are explained on the basis of *lanthanide contraction*.

AMINO acids play a greater role, as many of them are essential for human life. The complexes of several aminoacids with transition metal ions having incomplete d-subshell or f-subshell are reported in literature. Recently the author and his coworkers[1] have studied the interaction of La(III) and Ce(III) with glutamic acid in solution state by potentiometric titration technique. In continuation to the above studies the author now has taken to study the interaction of Pr(III), Nd(III) and Sm(III) with glutamic acid in the solution state. In this paper the stability constants, overall change in free energy (△G), enthalpy (△H) and entropy (△S) of Pr(III), Nd(III) and Sm(III) with glutamic acid at two different temperatures 30±0.1° and 40±0.1° are reported. In this communication an attempt is also made to establish and confirm the relationship between the rare-earth metal ions i.e. La(III), Ce(III), Pr(III), Nd(III) and Sm(III) etc.

Experimental

The nitrate salts of Pr(III), Nd(III) and Sm(III) were dissolved in conductivity water. The metal content of the solutions were gravimetrically estimated by precipitating the metal as metal oxalate and then ignited as metal oxide[1,2]. Standard carbonate free NaOH was used for potentiometric titrations. The glutamic acid used was in the form of mono-sodium glutamate. All the chemicals used were Anal-R (B.D.H. or equivalent).

The experimental procedure involved a series of *p*H-titrations of glutamic acid with standard NaOH solution in the absence and presence of metal ions at 30° and 40° in a constant temperature water-bath where the temperature was electrically controlled with in 0.1°. In all the titrations, volume (50 ml.) and ionic strength (0.1 M KCl) were kept constant. Other experimental details were already explained by the author in previous papers[3,4].

Results and Discussions

At different *p*H, the horizontal distances between the curves in absence and presence of metal ions, measure quite accurately the additional base consumed due to complex formation, i.e.,

$$M^{3+} + NaG.H \longrightarrow NaG : M^{2+} + H^{+}$$

(Where M^{3+} denotes rare-earth metals and NaG.H denotes mono-sodium glutamate).

Therefore at various *p*H, the different $\bar{n}$ and $\log\left(\frac{1}{A}\right)$ i.e., log K values were obtained for each metal at 30±0.1° and 40±01° by integral method of Calvin-Bjerrum[5,6,7] as adopted by Irving and Rossotti[8]. The different $\bar{n}$ and log K values so obtained were plotted and metal-ligand stability constants were read directly from graphs at $\bar{n}=0.5$ for 1 : 1, metal-ligand vatis. The ratio of metal-ligand interaction was also determined by conductometric titration as adopted by Job[9].

The metal-ligand stability constant of rare-earth metal ions with glutamic acid and thermodynamic parameters i.e., change in free energy (△G), enthalpy (△H) and entropy (△S) are reported in the table.

On going through the values of different constants for La(III), Ce(III), Pr(III), Nd(III) and Sm(III) from author's another paper[1] and the table it is evident that the order of stability constants follow the well established order i.e.,

La(III) < Ce(III) < Pr(III) < Nd(III) < Sm(III)

The above mentioned elements have partly filled f-subshells and therefore they are also known as inner transition metals. Since the f-orbitals are deep

TABLE—1 METAL-LIGAND STABILITY CONSTANTS AND THERMODYNAMIC PARAMETERS OF THE COMPLEXES AT μ = 0.1KCl

		$30 \pm 0.1°$	$40 \pm 0.1°$
Metal Ligand Stability Constant log K	Pr(III)	3.855	3.702
	Nd(III)	3.956	3.814
	Sm(III)	4.087	3.955
Change in free energy (ΔG) in KCal./Mole.	Pr.(III)	—5.346	—5.303
	Nd(III)	—5.475	—5.449
	Sm(III)	—5.667	—5.635
Change in enthalpy (ΔH) in KCal./Mole.	Pr(III)	—6.639	For the difference of 10°
	Nd(III)	—6.162	
	Sm(III)	—5.772	
Change in entropy (ΔS) in Cal/degree/Mole.	Pr(III)	—4.268	—4.269
	Nd(III)	—2.268	—2.237
	Sm(III)	—0.345	—0.438

seated and all the f-electrons have the same radial distribution, addition of electrons cannot change the size of the elements distinctly. Therefore in these inner transition metals (lanthanides) the difference in the values of stability constant, if any, is mainly due to *lanthanide contraction*. Similar types of behaviour for lanthanide complexes were also observed by several other investigators with different other complexing agents [10-13].

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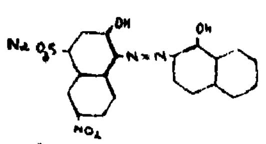
Thermodynamic Study of the Complexation Reaction of Some Solochrome Dyes with Lanthanum, Cerium, Thorium and Uranium

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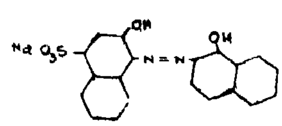
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The thermodynamic parameters for the complexation of four solochrome dyes viz., Solo yellow 2 GS, Solo Black WDFA, Solo 6 BN and Solo Fast Navy 2 RS, with lanthanum, cerium, thorium and uranium have been determined potentiometrically, at 28° and 44° and at an ionic strength of $\mu = 0.1$, in aqueous solutions. The step wise values of $\triangle G$, $\triangle H$ and $\triangle S$ have also been evaluated.

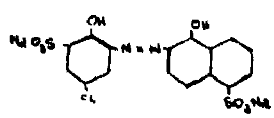
A vast variety of metal-dye complexes are employed commercially, amongst which, azo dyes are the ones most extensively used[1]. Two types of azo dyes are most important : (i) the azo salicylic acid and (ii) O-O'-dihydroxy azo dyes. In the present communication, we report the results of our investigations on the thermo-dynamic parameters of complexation of four such azo dyes (also called solochrome dyes) with lanthanum, cerium. thorium and uranium. The names and structures of the dyes are given below :



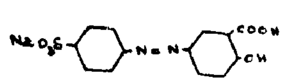
Solochrome Black WDFA



Solochrome 6BN



Solochrome Fast Navy 2RS



Solochrome Yellow 2GS

Experimental

Standard carbonate free potassium hydroxide[2] was used for potentiometric titrations. $HClO_4$ (Anala R, BDH) was used in all titrations. Solutions of lanthanum(III) chloride, cerium(IV) nitrate, thorium(IV) nitrate and uranyl(VI) acetat e $[UO_2(CH_3COO)_2\ 2H_2O]$ (all BDH materials) were prepared in water distilled from alkaline potassium permanganate solution and then redistilled twice and their strengths determined as usual.[2,3]

The solochrome dyes were obtained from ICI, India. They were purified by recrystallisation from 50% ethanol, dried over silica gel and tested for their purity by chromatography.[4] Solutions of the dyes were prepared in double distilled water from weighed amount and allowed to stand overnight before use. The solution of Solo 6 BN was prepared in 5% ethanol.

pH measurements were carried out on a battery, operated bench type cambridge pH meter, using glass and calomel electrodes. The pH meter was calibrated using standard buffers. The titrations were carried out in a thermostated water bath at 20° ± 0.1° and 44° ± 0.1°.

Procedure :

The following solutions (total volume 20 ml) were titrated pH meterically against 0.1 *M* KOH.

(i) 5.0 ml of 0.0392 $M HClO_4$

(ii) 5.0 ml of 0.0392 *M* $HClO_4$ + 5.0 ml of 0.01 to 0.005 *M* dye.

(iii) 5.0 ml of 0.00392 *M* $HClO_4$ + 5.0 ml of 0.01 to 0.005 *M* dye + 5.0 ml of .002 *M* Metal.

A constant ionic strength of 0.1 was maintained in each titration by adding the requisite amount of KCl_4O.

The protonation and formation constants were determined by the Calvin Bjerrum method[5,6] as modified by Irving and Rossotti[7].

Results and Discussion

The "practical" proton-ligand stability constants for the dyes were calculated[7] by plotting $\bar{n}_A$

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versus *p*H and are summarised in Table 1.

TABLE—1 PROTON LIGAND STABILITY CONSTANTS OF SOLOCHROME DYES

Dye	T°C	$\log K_1^H$	$\log K_2^H$	$\log B_n^H$
Solochrome	20	9.85	-	9.85
Yellow 2GS	44	9.20	-	9.20
Solochrome	20	11.50	7.00	18.50
Black WDFA	44	10.90	6.50	17.40
Solochrome	20	11.10	7.15	18.25
6 BN	44	10.95	6.80	17.75
Solochrome	20	11.80	9.20	21.00
Fast Navy 2RS	44	10.80	9.50	20.30

The step wise stability constant of a complex is given by,

$$K_n = C_{ML_n} / C_{ML_{n-1}} \cdot C_L \quad (\text{where } n = 1, 2, ..N)$$

Where K_n represents the *nth* metal-ligand stability constant. The stedwise stability constant was obtained by us from a plot of $\bar{n}$ against *p*L. The value of $\bar{n}$, the average number of ligands attached per metal ion is given by,

$$\bar{n} = \frac{(V^{III} - V^{II})\ (N^{\circ} + E^{\circ})}{(V^{\circ} + V^{\ddagger})\ \bar{n}_A\ T_{CM^{\circ}}}$$

While the free ligand exponent, pL is given by,

$$pL = \log_{10} \left[\frac{\sum_{n=0}^{n=j} \beta_n^H\ (1/\text{anti}\log pH)^n (V^{\circ} + V^{III})}{(T_{OL^{\circ}} - \bar{n}\ T_{OM^{\circ}})\ V^{\circ}} \right]$$

TABLE—2 Formation Constants of Metal Complexes of Solochrome Dyes

Dye	T°	La(III) Log K_1	La(III) Log K_2	La(III) Log β_2	Ce(IV) Log K_1	Ce(IV) Log K_2	Ce(IV) Log β_2	Th(IV) Log K_1	Th(IV) Log K_2	Th(IV) Log β_2	U(VI) Log K_1	U(VI) Log K_2	U(VI) Log β_2
Solo Y-2GS	20	8.7	-	8.7	9.3	8.4	17.7	9.4	7.2	16.6	8.2	-	8.2
	44	8.5	-	8.5	8.9	8.0	16.9	8.8	7.3	16.1	8.1	-	8.1
Solo B-WDFA	20	10.6	-	10.6	13.4	5.9	19.3	14.6	11.1	25.7	8.8	-	8.8
	44	10.6	-	10.2	13.7	6.3	20.0	14.5	12.2	26.7	8.9	-	8.9
Solo 6BN	20	10.7	-	10.7	13.9	8.2	22.1	14.7	8.9	23.6	9.7	-	9.7
	44	11.9	-	11.9	14.3	8.3	22.6	15.0	9.7	24.7	10.6	-	10.6
SoloF.Navy	20	12.4	-	12.4	16.1	11.4	27.5	18.0	13.3	31.3	11.2	-	11.2
2RS	44	12.5	-	12.5	17.3	10.6	27.9	19.7	12.5	32.2	11.4	-	11.4

TABLE—3 Free Energy of Metal-Dye Complexes (k cal mol^{-1})

Dye	T°	La(III) $-\Delta G_1$	La(III) $-\Delta G_2$	La(III) $-\Delta G$	Ce(IV) $-\Delta G_1$	Ce(IV) $-\Delta G_2$	Ce(IV) $-\Delta G$	Th(IV) $-\Delta G_1$	Th(IV) $-\Delta G_2$	Th(IV) $-\Delta G$	U(VI) $-\Delta G_1$	U(VI) $-\Delta G_2$	U(VI) $-\Delta G$
Solo Y-2GS	20	11.62	-	11.62	12.42	11.22	23.64	12.55	9.61	22.16	10.95	-	10.95
	44	12.28	-	12.28	12.86	11.56	24.42	12.72	10.55	23.27	11.70	-	11.70
Solo B-	20	14.16	-	14.16	17.90	9.97	27.87	19.50	14.83	34.33	11.75	-	11.75
WDFA	44	14.74	-	14.74	19.87	9.10	28.97	20.95	17.63	38.58	12.86	-	12.86
Solo 6 BN	20	14.29	-	14.29	18.57	10.95	29.52	19.64	11.89	31.53	12.95	-	12.95
	44	17.20	-	17.20	20.67	11.99	32.66	21.68	14.02	35.70	15.32	-	15.32
Solo F.	20	16.56	-	16.56	21.51	15.23	36.74	24.04	17.76	41.80	14.96	-	14.96
Navy 2RS	44	18.06	-	18.06	25.00	15.32	40.32	28.47	18.06	46.53	16.47	-	16.47

TABLE—4 Enthalpy of Metal-Dyes Complexe (in k cal mol^{-1})

Dye	La(III) ΔH_1	La(III) ΔH_2	La(III) ΔH	Ce(IV) ΔH_1	Ce(IV) ΔH_2	Ce(IV) ΔH	Th(IV) ΔH_1	Th(IV) ΔH_2	Th(IV) ΔH	U(VI) ΔH_1	U(VI) ΔH_2	U(VI) ΔH
Solo Y-2GS	-3.52	-	-3.52	-7.05	-7.05	-14.10	-10.58	1.76	-8.82	-1.76	-	-1.76
Solo B-WDFA	-7.05	-	-7.05	6.17	7.05	13.22	-1.76	19.41	17.64	1.76	-	1.76
Solo 6 BN	21.17	-	21.17	7.05	1.76	8.81	-5.29	14.11	19.40	15 88	-	15.88
Solo F. Navy 2RS	1.76	-	1.76	21.17	-14.11	7.06	30.00	-14.11	15.89	3.52	-	3.52

TABLE—5 Entropy Data on Metal-Dye Complexes (in Cal drgree^{-1} mol^{-})

DYE	T°	La(III) ΔS_1	La(III) ΔS_2	La(III) ΔS	Ce(IV) ΔS_1	Ce(IV) ΔS_2	Ce(IV) ΔS	Th(IV) ΔS_1	Th(IV) ΔS_2	Th(IV) ΔS	U(VI) ΔS_1	U(VI) ΔS_2	U(VI) ΔS
Solo Y-2GS	20	27.62	-	27.62	18.31	14.21	32.52	6.60	26.80	33.40	31.36	-	31.36
	44	27.62	-	27.62	18.31	14.21	32.52	6.72	27.77	34.49	31.36	-	31.26
Solo B-WDFA	20	24.24	-	24.24	81.41	58.12	139.53	61.01	106.82	167.83	46.14	-	46.14
	44	22.41	-	22.41	82.17	50.99	133.26	62.83	73.91	136 74	46.46	-	46.46
Solo-6BN	20	121.06	-	121.06	67.75	43.43	111.15	85.09	82.04	167.13	98.43	-	98.43
	44	66.80	-	66.80	87.47	43.40	130.88	85.09	88.76	173.85	98.43	-	98.43
Solo F. Navy	20	62.56	-	62.56	145.68	3.80	149.48	184.46	12.46	196.92	62.77	-	62.77
	44	62.56	-	62.56	145.68	3.83	149.48	184.46	12.46	196.92	63.11	-	63.11

The formation curves for lanthanum, cerium, Thorium and uranium with solo-chrome dyes are given in Figs. 1-4.

The estimated uncertainties in the thermodynamic parameters are ± 0.5 K Cal/mol in ΔH and ± 2 e u in ΔS.

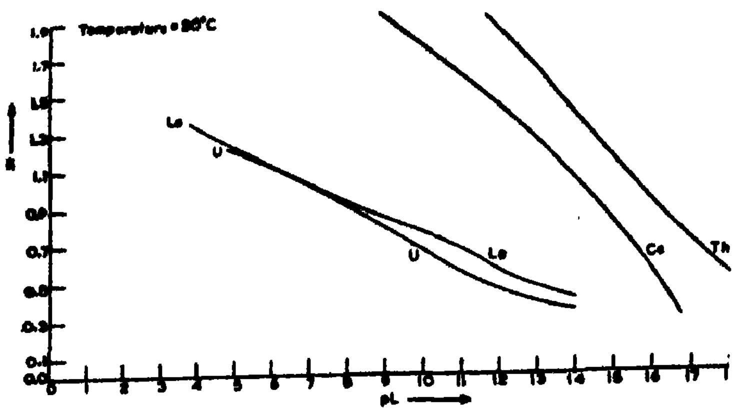


FIG. 1 – Formation curves of Solo.F.Navy 2RS complexes.

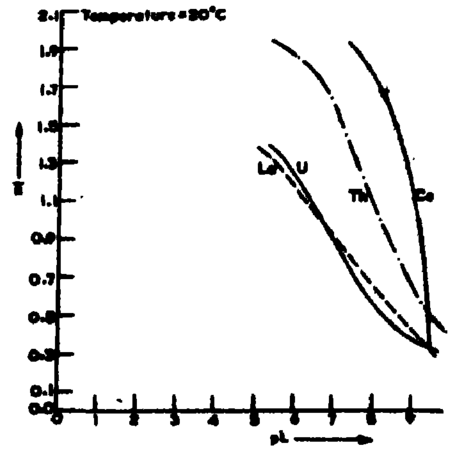


Fig. 4 Formotion curves of Solo. Y-1GS complexes.

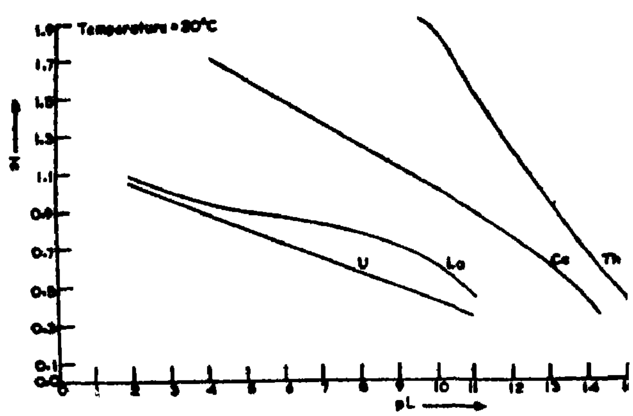


FIG. 2 – Formation curves of Solo. B.-WDFA complexes.

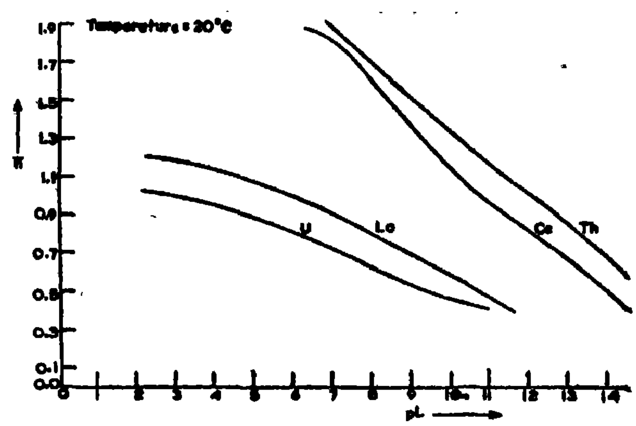


FIG. 3 – Formation curves of Solo. 6BN complexes.

The values of $\bar{n}$ were less than 1.5 for the complexes of lanthanum and uranium and did not exceed 2.0 in the case of cerium and thorium, thereby showing the formation of only 1 : 1 complexes in the former cases and both 1 : 1 and 1 :2 complexes in the latter cases. The values of the concentration, stability constants at an ionic strength $\mu = 0.1$ (Table 2), were used to calculate the thermodynamic parameters (Tables 3-5) from the following relations :

$$\Delta G = -RT \ln K$$

$$\ln K_2 . K_1 = \frac{\Delta H}{R} \frac{T_2 - T_1}{T_1 . T_2}$$

$$\text{and } \Delta G = \Delta H - T\Delta S$$

An examination of the stability constants (Table 2) shows that Solochrome yellow 2GS forms the least stable complexes while Solochrome fast Navy 2RS forms the most stable complexes. Further the values of log βn for Solo 6BN and Solo B. WDFA show that introduction of an NO_2 group (Electron withdrawing) lowers the stability of the resulting complex. Also the dyes with two OH groups (O-O' dihydroxy) form more stable complexes that the dyes with one OH group (Solo. Y-2GS) due to the formation of more stable ring across the azo bridging.

The stability of the complexes follows the order : Solo. Y-2GS < Solo. B-WDFA < Solo. 6 BN< Solo F. Navy 2RS

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Mixed Chelate Complexes of Manganese(II)

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Manganese(III) complexes like manganese *tris*-thiocarbamates, -acetylacetonates and -picolinates were reacted with heterochelates. Even though mixed chelate complexes were formed, surprisingly trivalent manganese was invariably reduced to divalent state. Analytical, molar conductance, magnetic susceptibility, infra red and electronic spectral data reveal that these heterochelate compounds are high spin manganese(II) complexes with presumably tetrahedral configuration.

DITHIOCARBAMATES are well known as Vulcanization accelerators in rubber industry and have also been patented as fungicides. Amongst them, the dithiocarbamates of manganese have been under controversial discussion in recent years. Especially, manganese(II) dithio-carbamates reported earlier[1-3] were contradicted [4,5] due to their ready susceptibility towards oxidation by air. They are reported to be stable only in inert atmosphere and are easily oxidised to manganese(III) in presence of atmospheric air. In case of manganese (III) complexes, attempts were made earlier to prepare some mixed chelate complexes[6-8] and study their structures in an environment of heteroatomic ligand field. In none of these complexes dithiocarbamate was present as bonded ligand. In view of this, we tried to prepare some mixed chelate complexes of manganese(III) containing dithiocarbamate and 8-hydroxyquinoline (ox), acetylacetone (acac) or picolinic acid (pyca). These reactions were found to produce only manganese(II) mixed chelates which was confirmed by analytical data, magnetic susceptibility and electronic spectra. The manganese(III) was found to be invariably reduced to manganese(II) when dithiocarbamate is one of the chelating group.

Experimental

The diethyl (Et_2dtc), piperidyl (Pipdtc) and morpholyl (Morphdtc) dithiocarbamates of manganese(III) were prepared by known methods[9,10]. *Tris* (acetylacetonato) manganese(III) was prepared as described by Jacob[11].

Preparation of mixed chelate complexes :

Mn(Et_2dtc)(ox), Mn(Pipdtc)(ox), Mn(Morphdtc)(ox)

Manganese *tris* thiocarbamates, *viz.* Mn(Et_2dtc)$_3$, Mn(pipdtc)$_3$ and Mn(Morphdtc)$_3$ were reacted separately with 8-hydroxyquinoline (ox) in 1 : 1 molar ratio in acetone medium. The resulting solution was refluxed for nearly 30 mts, when microcrystalline compounds separated out which were suction filtered, washed with acetone followed by ether and dried in *vacuo*.

Mn(acac)(Et_2dtc) ; Mn(acac)(Pipdtc)

To a chloroform solution of Mn(acac)$_3$ an ethanolic solution of sodium salt of diethyl or piperidyl dithiocarbamate (1 : 1 molar ratio) was added. Immediately the original dark colour of *tris*-acetylacetonate was discharged and a greyish white silky compound separated out. The contents were refluxed for a few minutes to ensure complete reaction. The separated compound was suction filtered, washed with ethanol followed by ether and dried in *vacuo*. The same compounds were obtained during the reverse process, when *tris*-dithiocarbamates of manganese(III) were reacted with acetylacetone in 1 : 1 molar ratio followed by dropwise addition of ammonia.

Mn(Pyca)(Et_2dtc), Mn(Pyca)(Pipdtc)

Tris-picolinatomanganese(III), Mn(Pyca)$_3$, was prepared by reacting methanolic solutions of manganese (III) acetate dihydrate and picolinic acid in 1 : 3 molar ratio. On stirring well a bright orange coloured shining microcrystalline compound separated out which was suction filtered, washed with methanol followed by ether and dried in *vacuo*.

Hot ethanolic solution of Mn(Pyca)$_3$ was treated with ethanolic solution of sodium salt of diethyl or piperidyl dithiocarbamate in 1 : 1 molar ratio and refluxed for one hour and cooled. Shining chatolate coloured compounds separated out which were suction filtered washed with ethanol followed by ether and dried in *vacuo*. The same compounds were obtained when *tris*-dithiocarbamates of manganese(III) were refluxed with picolinic acid in 1 : 1 molar ratio for 30 minutes.

Physical measurements :

All the complexes reported have elemental analyses, electrical conductivities, magnetic susceptibilities,

i.r. spectra and electronic spectra consistent with their formulations and these data are presented in Tables 1, 2 and 3. Manganese and sulphur were estimated by standard methods. The conductance measurements in nitrobenzene medium were carried out using Toshniwal conductivity bridge, type CL 0102 with a dip type cell. The magnetic susceptibility measurements at room temperature were carried out on solid specimens using Guoy method. Infrared spectra in the range 5000-650 cm^{-1} were recorded on nujol mull using Unicam SP-200 double beam spectrophotometer. The electronic spectra were recorded using Unicam SP-500 spectrophotometer. Since the compounds were not appreciably soluble in organic solvents, the nujol mull paper technique was used.

TABLE—1 ANALYTICAL, MELTING POINT, CONDUCTANCE AND MAGNETIC SUSCEPTIBILITY DATA OF MANGANESE(II) COMPLEXES

Compound	Colour	M.P. (°C)	% Mn Found/Calc.	% S Found/Calc.	Λ_M (mhos)	μ_{eff} (B.M.)
1. Mn(Et_2dtc) (ox)	dirty green	>300	15.69/15.82	18.39/18.45	3.8	5.96
2. Mn(Pipdtc) (ox)	dirty green	>300	14.99/15.30	17.92/17.84	3.6	5.96
3. Mn(Morphdtc) (ox)	Greenish yellow	>300	15.01/15.22	17.6 /17.74	3.9	5.93
4. Mn(acac) (Et_2dtc)	Greyishwhite	290	18.3 /18.20	21.0 /21.21	3.9	5.80
5. Mn(acac) (Pipdtc)	Greyish white	>300	17.6 /17.51	20.7 /20.44	3.7	5.76
6. Mn(Pyca) (Et_2dtc)	Shining chocolate	>300	16.71/16.89	19.53/19.72	3.5	5.85
7. Mn(Pyca) (Pipdtc)	Light yellow	>300	16.15/16.30	19.0 /19.03	3.4	5.79

TABLE—2 INFRARED ABSORPTION BANDS (CM^{-1}) OF MIXED CHELATE MANGANESE(II) COMPLEXES

Compound	dithiocarbamate			Oxine	acetylacetone		Picolinic acid
	ν(C-N)	ν_{as}(C-S)	ν_s(C-S)	ν(C-O)	ν(C-C)	ν(C-O)	ν_{as}(CO-O)
1. Mn(Et_2dtc) (ox)	1500s	1020w	710s	1095s			
2. Mn(Pipdtc) (ox)	1500s	1010s	710s	1097s			
3. Mn(Morphdtc) (ox)	1500vs	1010s	710s	1097s			
4. Mn(acac) (Et_2dtc)	1520s	1000s	700s		1600vs	1520s	
5. Mn(acac) (Pipdtc)	1520s	1005s	710s		1600vs	1520s	
6. Mn(Pyca) (Et_2dtc)	1520w	1002s	738s				1640vs, 1600vs, 1578s
7. Mn(Pyca) (Pipdtc)	1510w	1010s	738s				1640s, 1605s, 1580s

s=sharp, vs – very sharp, w = weak.

TABLE—3 ELECTRONIC ABSORPTION SPECTRA OF MIXED CHELATE MANGANESE(II) COMPLEXES.

Compound	Absorption max. (cm^{-1})			
1. Mn(Et_2dtc) (ox)	26315	23530	22470	20200
2. Mn(Pipdtc) (ox)	26315	23570	22990	20000
3. Mn(Morphdtc) (ox)	26315	23570	22730	20000
4. Mn(acac) (Et_2dtc)	27030	23570	22730	20410
5. Mn(acac) (Pipdtc)	27030	23530	22470	20000
6. Mn(Pyca) (Et_2dtc)	27030	23570	22730	20000
7. Mn(Pyca) (Pipdtc)	26315	23530	22470	20000

Results and Discussion

An important property of the dithiocarbamates as ligands is their capacity for stabilizing metal ions in a wide range of oxidation states. It was reported that manganese(III) dithiocarbamates are both readily oxidised and reduced to manganese(IV) and manganese(II)[12]. In the present case, the tris-dithiocarbamates were found to undergo reduction to divalent state on the introduction of a heterochelate group in the complex.

All the complexes are non electrolytes as evidenced by low molar conductance values (Table 1) of the 10^{-3}M solutions in nitrobenzene medium. Convincing support for the divalent state of manganese in the above complexes is obtained from their magnetic suscepticility values. The dithiocarbamate complexes of manganese(III) have been reported to have magnetic moments in the range 4.4-4.9 B.M.[13, 14]. But manganese(II) compounds usually have spin-only magnetic moments of *ca.* 5.9 B.M. (high spin d^5 configuration, $S=5/2$) which are temperature independent[15] unless antiferromagnetism is present. The complexes under present investigation give rise to magnetic moment values of 5.76-5.96 B.M. (Table 1) indicating the presence of 5 unpaired electrons which are quite in conformity with a spin-free manganese(II) state. These values of magnetic moment cannot otherwise be explained in terms of manganese(III) ($3d^4$ configuration).

Infrared spectra :

The relevant infrared absorption bands due to the coordinated chelates of the complexes with their possible assignments are given in Table 2. Many bands due to 8-hydroxyquinoline and picolinic acid are found to be superimposed over the bands of

dithiocarbamates. However, the most characteristic bands which could be distinctly assigned were given in the table. The ν (C—N) and ν (C—S) bands due to dithiocarbamates indicate clearly that they are coordinated to the metal ion through both the sulphur atoms[9,10]. The ν (C—O) for 8-hydroxyquinoline (ox) obtained at 1095-1097 cm^{-1} indicates that it is coordinated to the metal ion through nitrogen and oxygen atoms[16]. In the acetylacetonato complexes, the bands due to ν (C⎯C) and ν (C⎯O) were obtained at 1600 and 1520 cm^{-1}, respectively as expected, indicating the presence of coordinated acetyl acetone group[17]. In case of picolinic acid complexes, the band due to free carboxyl group at 1710 cm^{-1} was found to be absent. Other bands due to ν_{as} (COO) and pyridine ring were found to be present as observed by Fowles *et.al*[18]. This suggests that picolinic acid is coordinated to the metal ion through oxygen and nitrogen atoms.

Eletcronic Spectra :

The dithiocarbamate complexes of manganese (III) are found to give bands[9] at ~27800, ~20000 and ~ 16000 cm^{-1}. In the complexes now studied, no band at ~16000 cm^{-1} could be obtained which indicates the absence of manganese(III) species in the complexes. On the other hand, all the absorption bands recorded for the present complexes (Table 3), can be satisfactorily assigned on the basis of a tetrahedral geometry for manganese(II). Forster and Goodgame have studied[19] the electronic spectra of $[Et_4N]_2$ $[Mn(NCO)_4]$ and found transitions from $^6A_1$ ground state occuring at *Ca.* 20400 [$\rightarrow {}^4T_1(G)$], 22400 [$\rightarrow {}^4T_2(G)$], 23300 [$\rightarrow$4E, $^4A_1(G)$], 27500 and *Ca.* 26000 cm^{-1}. They have suggested a tetrahedral configuration for the above compound on the basis of their results. The bands obtained in the present investigation are similar and definitely indicate a tetrahedral geometry to all the complexes now reported.

It is therfore interesting to find that even though our efforts to prepare some mixed chelate complexes of trivalent manganese did not succeed, we could characterise mixed chelate complexes of divalent manganese. These are very stable whilst $Mn(dtc)_3$ is susceptible to aerial oxidation.

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Complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with Substituted Thiocarbamides

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Sixteen complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) have been synthesised using N-*o*-hydroxyphenyl-N′-phenyl, N-N′-di-(*o*-hydroxyphenyl), N-*o*-hydroxyphenyl and N-*o*-carboxyphenyl thiocarbamides as ligands and characterised on the basis of analysis, conductance, magnetic susceptibility, i.r. and electronic spectral studies. Complexes have the composition $[ML_2]$. (M=Co(II), $[MLCl(H_2O)_2]$ (M=Ni(II), [MLCl] (M=Cu(II), Zn(II), Cd(II) and Hg(II).

THIOUREA has been used extensively as a ligand to study the affinity of the sulfur atom towards different metal ions. Many simple complexes of thiourea[1-3] and mixed ligand complexes[4-6] containing thiourea and nitrogen donor ligands have been reported earlier. Even though less number of complexes with substituted thiourea as ligands have been investigated[7,8], Zn(II) and Hg(II) compounds have been well studied. Inspite of the extensive work in this field, attempts have not been made to study complexes ot thiocarbamide ligands containing other potential donor sites (*viz* oxygen or nitrogen) in addition to the sulfur atom. It was, therefore thought worthwhile to synthesise some new substituted thiocarbamides and study their complexation behaviour towards a series of divalent metal ions. In an earlier communication[9], we reported complexes of Co(II), Ni(II), Zn(II) and Hg(II) with a hydroxy and carboxy substituted thiocarbamide. This communication presents a number of complexes. of N-*o*-hydroxyphenyl-N′-phenyl and N-N′-di (*o*-hydroxyphenyl) thiocarbamide with Co(II), Ni(II), Cu(II), Zn(II), Cg(II) and Hg(II) ions and complexes of N-*o*-hydroxyphenyl and N-*o*-carboxyphenyl thiocarbamide with Cu(II) and Cd(II) ions.

Experimental

All the chemicals used were of AnalaR grade.

Preparation of N-o-hydroxyphenyl-N′-phenyl thiocarbamide :

To an ethanolic solution of *o*-aminophenol (4.36 g), phenyl isothiocyanate (5.40 ml) was added and the mixture was refluxed for 15 minutes over a water-bath. On cooling, crystalline compound of the corresponding thiocarbamide separated out which was then filtered, washed in ethanol and dried in *vacuo*.

Preparation of N-N′-di-(o-hydroxyphenyl) thiocarbamide :

To an ethanolic solution of *o*-aminophenol (4.36 g.), carbondisulphide (3 ml) and potassium hydroxide (2 g.) were added and refluxed for half an hour over waterbath, and then the hot solution was poured into ice-cold water. Then the hot solution was made slightly acidic by adding conc. HCl, when reddish-brown precipitate was separated out which was filtered, washed with water and crystallised from rectified spirit.

The synthesis of N-*o*-hydroxyphenyl and N-*o*-carboxyphenyl thiocarbamide has been described in our earlier communication[9].

Preparation of complexes :

Ethanolic solution of metallic chlorides were treated with ethanolic solutions of N-*o*-hydroxyphenyl-N′-phenyl and N-N′-di-(*o*-hydroxyphenyl) thiocarbamides and ethanolic solution of Cu(II), Cd(II), chlorides weret reated with N-*o*-hydroxyphenyl and N-*o*-carboxyphenyl thiocarbamides in the dimethyl formamide in stoichiometric ratios followed by the dropwise addition of ammonie when metal chelates separated out which were then filtered, washed with ethanol followed by ether and dried in *vacuo*.

Metals, nitrogen and sulfur in the complexes were estimated by standard methods. Conductance was measured in M/1000 acetone solution of the complexes using Toshniwal conductivity bridge. Magnetic susceptibility measurements were made over solid specimens by Gouy method using $Co[Hg(SCN)_4]$ as calibrant. IR spectra were measured on KBr phase by a Perkin Elmer-221 spectrophotometer in the 200-4000 cm^{-1} range. Electronic spectra were recorded in M/100 chloroform solution of the

complexes using Hilger-Watt Uvispeck spectrometer. Analytical data are recorded in Table-1 and spectral data in Table-2.

IR spectra have been of considerable help in determining the bonding sites. There are three bonding sites very near to each other, *viz.* the hydroxyl or carbonyl oxygen, sulfur of the thiocarbonyl group and nitrogen of the amino group. In the ligands the alcoholic C-O vibration occurs around 1250-1260 cm^{-1}, which should usually occur in the 1000-1300 cm^{-1} range in case of alcohols. In addition, there are both broad and sharp bands in the 3300-3500 cm^{-1} region due to O-H and N-H stretching vibrations respectively. Usually thiocarbonyl absorption occurs[10] around 1020-1250 cm^{-1} *region, several* other bands appear in the 1500-700 cm^{-1} region due to interaction between C=S and C-N stretching when the C=S group is attached to a nitrogen atom. A prominent sharp band has appeared at ~ 700 cm^{-1} as in case of simple thiourea.

In case of complexes, C-O and C=S stretching frequencies definitely shift to lower frequency region indicating bonding at these sites. In addition, the position of -NH stretching band also *shifts as there is*

TABLE—1 ANALYSIS, CONDUCTANCE AND MAGNETIC SUSCEPTIBILITY DATA

Compound	% of metal		% of N		% of S		Δ mhos cm^2	μ_{eff} (B.M.)
	Found	Reqd.	Found	Reqd.	Found	Reqd.		
$[CoL_2]$	10.38	10.77	10.03	10.23	11.48	11.70	8.0	5.00
$[CoL'_2]$	9.85	10.23	9.57	9.80	10.93	11.20	7.5	5.10
$[NiLCl(H_2O)_2]$	14.95	15.37	7.16	7.33	8.21	8.33	8.0	3.10
$[NiL'Cl(H_2O)_2]$	14.72	15.09	7.14	7.23	8.08	8.21	8.5	3.00
[CuLCl]	18.14	18.55	7.92	8.17	9.17	9.34	8.2	1.81
[CuL'Cl]	17.67	17.92	7.64	7.09	8.87	9.02	10.1	1.83
[CuL"Cl]	23.62	23.88	10.27	10.49	11.72	11.99	7.8	1.78
[CuL‴Cl]	21.18	21.58	9.36	9.50	10.60	10.86	7.5	1.81
[ZnLCl]	18.52	18.98	7.97	8.13	9.14	9.29	9.6	-
[ZnL'Cl]	17.94	18.25	7.69	7.84	8.54	8.82	8.8	-
[Cd LCl]	28.28	28.71	6.94	7.15	7.93	8.17	11.5	-
[CdL'Cl]	27.45	27.86	6.79	6.94	7.68	7.93	8.8	-
[CdL"Cl]	35.21	35.63	8.59	8.87	8.93	10.14	9.4	-
[CdL‴Cl]	29.94	30.13	7.25	7.49	8.36	8.57	11.2	-
[HgLCl]	41.46	41.32	5.54	5.87	6.32	6.67	9.2	-
[HgL'Cl]	40.53	40.86	5.47	5.69	6.37	6.51	9.5	-

TABLE—2 IR AND ELECTRONIC SPECTRAL DATA

Compound	ν (C-O)	ν(C-S)	ν(M-O)	ν(M-N)	ν(M-S)	ν(M-Cl)	νmax K. K.(ε)
$[CoL_2]$	1240	1090	460	375	270	-	20.9(18), 18.9(29), 18.0(16)
$[CoL'_2]$	1250	1100	450	380	260	-	20.8(18), 19.0(30), 7.9(15)
$[NiLCl(H_2O)_2]$	1240	1095	440	375	270	230	8.9(7), 13.5(7), 25.2(15)
$[NiL'Cl(H_2O)_2]$	1250	1090	445	370	265	220	8.9(6), 13.6(6.5), 25.0(16).
[CuLCl]	1245	1085	440	370	275	225	-
[CuL'Cl]	1250	1090	450	375	270	230	-
[CuL"Cl]	1240	1090	440	380	290	230	-
[CuL‴Cl]	1250	1100	445	370	260	220	-
[ZnLCl]	1245	1045	420	360	260	225	-
[ZnL'Cl]	1255	1100	425	370	270	230	-
[CdLCl]	1250	1090	430	380	270	230	-
[CdL'Cl]	1245	1085	420	375	280	230	-
[CdL"Cl]	1240	1100	425	370	280	235	-
[CdL‴Cl]	1240	1100	420	360	275	220	-
[HgLCl]	1240	1100	460	375	275	220	-
[HgL'Cl]	1250	1095	455	380	260	225	-

LH = N-*o*-hydroxyphenyl-N'-phenyl thiocarbamide, L'H = N,N'-di-(*o*-hydroxyphenyl) thiocarbamide, L"H = N-*o*-hydroxyphenyl thiocarbamide, L‴H = N-*o*-carboxyphenyl thiocarbamide.

Results and Discussion

Complexes reported in the present investigation have the composition $[ML_2]$ (M=Co(II), $MLCl(H_2O)_2$ (M=Ni(II), [MLCl] (M=Cu(II), Zn(II), Co(II) and Hg(II). Cobalt complexes are pink, nickel complexes are green, copper complexes are either blue or green and Zn(II), Cd(II) and Hg(II) complexes are white. These have fairly low melting points and the conductance values in acetone medium are low indicating nonelectrolytic nature of the complexes. Magnetic moments (at 25°) of cobalt and nickel complexes show the presence of three and two unpaired electrons respectively indicating a high spin octahedral configuration. Copper complexes are paramagnetic with the presence of one unpaired electron.

a splitting when nitrogen is bonded to the metal ion. The broad absorption band due to O-H stretching vibration disappears in case of Co(II), Cu(II) Zn(II), Cd(II) and Hg(II) complexes but is observed in case of nickel complexes due to the presence of coordinated water. In complexes with N-N′-di-*o*-hydroxy phenyl thiocarbamide, O-H stretching band is observed in all cases as one -OH group remains free. Evidence in favour of three bonding sites is further substantiated by observations of M-O, M-S and M-N stretching bands in the far infrared spectra of the complexes[11]. In addition, a low frequency band has been observed around 220-230 cm^{-1} in case of complexes where halogen is present. Thus from analysis, conductance, and IR spectral studies, Zn(II), Cd(II) and Hg(II) complexes are presumably tetracoordinated involving a tetrahedral environment around the metal ions.

In the electronic spectra of nickel complexes, three absorption bands appear around 9000, 13000 and 25000 cm^{-1} region assignable[12] to $^3A_{2g} \rightarrow {}^3T_{2g}$ (F), $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) transitions respectively. Molar absorptivity values are low in conformity with the octahedral configuration of the complexes. Cobalt (II) complexes also exhibit three absorption bands in the 20000, 19000 and 8000 cm^{-1} region attributable to $^4T_{1g} \rightarrow {}^4T_{1g}$(P), $^4T_{1g} \rightarrow {}^4A_{2g}$ (F) and $^4T_{1g} \rightarrow {}^4T_{2g}$ (P) transitions respectively. Low extinction coefficient values support the octahedral stereochemistry of these complexes. In the electronic spectra of Cu(II) complexes one broad absorption band appeared around 15000-16000 cm^{-1} region indicating a planar configuration for these complexes[12].

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Formation Constants of Some Tl(I)-Halogen Substituted Salicylates and Effect of Halogen Atom on the Stability

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Formation constants of Tl(I) complexes with 5-chloro, 5-bromo and 5-iodo substituted salicylic acid were found to be in the order of Tl(I)-5ClSA > Tl(I)-5BrSA > Tl(I)-5ISA, where as protonation constants (Basicity) are in the order of 5ISA > 5BrSA > 5ClSA. This may be attributed to the steric effect of different halogen atoms in each case.

SURVEY of literature reveals that no work has been done on complexing tendencies of Tl(I) with 5-halogen substituted salicylic acid. In continuation of the previous work on the effect of nitro group on the formation constants of Tl(I)-salicylate complexes[1-3], present investigation deals with the effect of halogen atoms on the formation constants of Tl(I)-salicylates. Formation constants of Tl(I)-5-halogen substituted salicylates *viz.* 5-chloro salicylates [Tl(I)5CLSA], 5-bromo salicylates [Tl(I) 5-BrSA], and 5-iodo salicylates [Tl(I)5-ISA] have been determined at 30°, using different computational methods *viz.* half-integral (HI), linear plot (LP) and point-wise calculation (PC) methods. Refined values are obtained by the method of least-squares(LS). Proton ligand formaton constants required for the purpose, are also determined under the same experimental conditions using the aforesaid methods.

To study the effect of the halogen atom on the protonation and formation constants of Tl(I)-salicylates, proton ligand formation constants and formation constants of salicylic acid (SA) with Tl(I), have also been determined under the same experimental conditions and already reported[6].

Experimental

All the chemicals used were of B.D.H. Analar grade. Polymetron model CL-41 pH-meter was used for pH-metric titrations conducted at 30°. Measurments were made with an accuracy of ± 0.05 pH units and the reproducibility of the readings wes of the same order.

pH-metric titrations of solution (i) free $HClO_4$, (ii) free $HClO_4$ + ligand and (iii) free $HClO_4$ + ligand + Tl(I), were performed in 50% (v/v) aqueous ethanol medium against standard NaOH solution while maintaining the ionic strength at 0.1 *M* $NaClO_4$.

The experimental set up and the method of calculation is the same as described earlier.

Proton ligand formation constants and formation constants of complexes :

The Irving-Rossotti expression[4] was used for the calculation of $\bar{n}_A$, $\bar{n}$ and p(L). In the calculation of $\bar{n}_A$, $\bar{n}$ and p(L), the concentrations were corrected for the changes in volume as a result of addition of alkali during titrations. A series of values of $\bar{n}_A$, $\bar{n}$ and p(L) corresponding to different B-values (pH meter readings) were calculated and the formation curves for the ligands and the complexes were obtained by plotting $\bar{n}_A$ vs pH (B-value) and $\bar{n}$ vs. p(L) respectively. The values of log K_1^H, log K_2^H and log K_1, log K_2 for each case were recorded directly from the respective formation curve by half integral method. The values of pH (B-values) at $\bar{n}_A = 0.5$ and 1.5 correspond to values of log K_1^H, and log K_2^H respectively, where as values of p(L) at $\bar{n}=0.5$ and 1.5 correspond to log K_1 and log K_2 respectively. Proton ligand formation constants and formation constants of complexes are calculated by linear plot and point-wise calculation method using equation :

$$\log K_n^H = B + \log \frac{\bar{n}_A - (n-1)}{n - \bar{n}_A}$$

and

$$\log K_n = p(L) + \log \frac{\bar{n} - (n-1)}{n - \bar{n}}$$

$$(\text{as } \log K_n = p(L)_{n-\frac{1}{2}})^5$$

in the two regions where $\bar{n}_A$ or $\bar{n}$ is >1 and <1.

Refined values of formation constants are obtained by the method of least squares. Values are recorded in Table-1, 2 and 3.

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TABLE—1

Tl(I)-5-ClSA					Tl(I)-5-BrSA					Tl(I)-5-ISA				
B	n̄	p(L)	Point-wise		B	n̄	p(L)	Point-wise		B	n̄	p(L)	Point-wise	
			log n̄/(1-n̄)	log K_1				log n̄/(1-n̄)	log K_1				log n̄/(1-n̄)	log K_1
6.0	0.353	9.08	−0.26	8.81	6.2	0.336	8.85	−0.30	8.55	6.6	0.372	8.44	−0.23	8.21
6.2	0.425	8.84	−0.13	8.71	6.4	0.388	8.60	−0.20	8.50	6.8	0.444	8.21	−0.10	8.11
6.4	0.504	8.57	+0.01	8.58	6.6	0.441	8.38	−0.10	8.28	7.0	0.536	7.97	−0.06	8.03
7.0	0.703	7.88	+0.37	8.25	7.0	0.578	7.90	+0.14	8.04	7.2	0.611	6.74	+0.20	7.93
7.6	0.852	7.12	+0.76	7.88	7·2	0.664	7.67	+0.30	7.97	7.4	0.682	7.49	+0.33	7.82
8.0	1.001	6.75	log(n̄-1)/(2-n̄)	log K_2	8.0	1.020	6.72	log(n̄-1)/(2-n̄)	log K_2	8.2	0.955	6.56	log(n̄-1)/(2-n̄)	log K_2
8.4	1.155	6.22	−0.74	5.48	9.0	1.323	5.56	−0.32	5 24	8.8	1.171	5.85	−0.69	5.17
8.6	1.203	5.99	−0.59	5.40	9.2	1.466	5.33	−0.06	5.28	9.0	1.259	5.62	−0.46	5.16
8.8	1.302	5.76	−0.36	5.39	9.4	1.550	5.09	+0.09	5.18	9.2	1.354	5.29	−0.26	5.02
9.2	1.442	5.29	−0.10	5.18	9.6	1.693	4.88	+0.35	5.23	9.4	1.433	5.14	−0.12	5.02
9.4	1.563	5.04	+0.11	5.15	9.8	1.824	4.66	+0.67	5.33	9.8	1.636	4.69	+0.24	4.93

TABLE—2 PROTON LIGAND FORMATION CONSTANTS OF LIGANDS

Method	5-ClSA			5-BrSA			5-ISA			SA[6]		
	log K_1^H	log K_2^H	log K_B^H	log K_1^H	log K_2^H	log K_B^H	log K_1^H	log K_2^H	log K_B^H	log K_1^H	log K_2^H	log K_B^H
HI*	11.38	2.56	13.94	11.83	2.68	14.51	11.55	3.00	14.55	11.40	3.21	14.61
LP	11.58	2.60	14.18	11.51	2.66	14.17	11.76	2.99	14.75	12.00	3.20	15.20
PC	11.88	2.70	14 58	11.60	2.67	14.27	11.76	3.00	14.76	12.29	3.20	15.45
Average	11.61	2.62	14.23	11.65	2.67	14.32	11.69	3.00	14.69	11.90	3.20	15.10

*Values of log K_1^H are calculated from log K_B^H

TABLE—3 FORMATION CONSTANTS OF TL(I)-COMPLEXES

Method	Tl(I)-5-ClSA			Tl(I)-5-BrSA			Tl(I)-5-ISA			Tl(I)-SA[6]		
	log K_1	log K_2	log K_B	log K_1	log K_2	log K_B	log K_1	log K_2	log K_B	log K_1	log K_2	log K_B
HI	8.55	5.15	13.70	8.28	5.20	13.48	8 00	5.00	13.00	8.95	5.00	13.95
LP	8.55	5.20	13.75	8.21	5.14	13.35	8.04	5.06	13.10	8.95	5.02	13.97
PC	8.45	5.32	13.77	8 27	5.25	13.52	8.02	5 04	13.06	8.75	5.07	13.82
LS	8.50	5.26	13.76	8.29	5.24	13.53	8.02	5.03	13 05	8.94	5.12	14.06
Average	8.51	5.23	13.74	8.26	5.21	13.47	8.02	5.03	13.05	8.90	5.05	13.95

Results and Discussion

Values of log K_1^H, log K_2^H and log K_1, log K_2 of 5-halogen substituted salicylic acid and their complexes with Tl(I), are recorded in Table 2 and 3.

The ratio of log K_1/K_2 is positive in all the cases. A bigger difference between log K_1 and log K_2 is because of possible steric hindrance on the linking of the second ligand molecule.

In view of very low concentration (1×10^{-4} *M*) of Tl(I) used in the titration, formation of polynuclear complexes may be ignored. Titrations performed using different ratios of metal to ligand, showed that the stability constants are independent of metal ion concentration in all the cases.

In all the cases n̄ value never exeeds 1.85, indicating thereby formation of only 1 : 1 and 1 : 2 complexes. Estimation of elements in the complexes isolated, also indicate 1 : 2 ratio of metal to ligand in all the cases.

Effect of halogen atom :

The order of K_1^H of the ligands used in the present investigation (Table-2) is :

$$SA > 5\text{-}ISA \approx 5\text{-}BrSA \approx 5\text{-}CISA$$

and that of log K^H_{1a} is :

$$SA > 5\text{-}ISA > 5\text{-}BrSA > 5\text{-}CISA$$

where log K^H_1 represents protonation of phenoxide group and log K^H_2 protonation of carboxylate group. The order is in agreement with the order of inductive effect and resonance effect of the halogen atoms in each case[7].

The order of overall basicity (log K^H_B) is :

$$SA > 5\text{-}ISA > 5\text{-}BrSA > 5\text{-}CISA$$

The order of formation constants of Tl(I)-complexes (Table-3) is :

$$Tl(I)\text{-}SA > Tl(I)\text{-}5\text{-}CISA > Tl(I)\text{-}5\text{-}BrSA > Tl(I)\text{-}5\text{-}ISA$$

The order is not similar to the order of basicity of ligands but is similar to the order of the size of the halogen atoms :

$$I > Br > Cl$$

Hence this may be attributed to the steric hindrance of the halogen atoms[8], which is expected for Tl(I) ion because of its bigger size in comparision to proton of very small size.

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Spectrophotometric Studies of the Ti(IV) Complex with N-Benzoyl N-*meta*-Sulphonatophenylhydroxylamine

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Like Fe(III), Ti(IV) also forms water soluble but yellow coloured complex with *N*-benzoyl-*N*-meta-sulphonatophenylhydroxylamine in the *p*H range 1.5-2.5. The absorbances were measured at 410 nm. The yellow complex obeys Beer's law from 4 to 14 ppm; the optimum range, as evaluated from the standard curve, being 5 to 14 ppm of Ti and the relative error, as calculated from the Ayres' equation is 2.72%. Due to the highly dissociated nature of the complex a large excess of the reagent is to be used for the spectrophotometric study and as a result the composition of the yellow complex could not be determined.

PREPARATION of N-benzoyl-N-*meta*-sulphonatophenylhdroxylamine and spectrophotometric setudis of Fe(III) complexes with this reagent have been reported earlier[1]. This reagent also forms water soluble Ti(IV), V(V) and U(VI) complexes. In this paper is reported an attempt made to study the Ti(IV) complex. It has also been noticed that Ti(IV) can be estimated in the presence of Fe(III) by masking it with ascorbic acid. Ti(IV) can also be estimated with sufficient accuracy in the presence of Fe(III) and V(V) with the use of NH_2OH, HCl or NH_2NH_2, H_2SO_4 as reducing agetn.

Apparatus :

Optical densities were measured with a Hilger UVISPECK spectrophotometer using 1 cm. quartz cells against water as blank. The *p*H values of the solutions were measured with an 'Elico' *p*H meter (L 1-10).

Standard Ti(IV) solution :

A.R. potassium titanyl oxalate was digested with $(NH_4)_2SO_4$ and concentrated H_2SO_4, boiled for 10-15 mins. allowed to cool, poured into a 500 ml measuring flask and diluted upto the mark. Its titanium content was then determined from an aliquot portion by precipitating with ammonia or by BPHA[2] (N-benzoyl-N-phenylhydroxylamine) and igniting to oxide. The solution was afterwards diluted to give a solution containing 100 ppm of Ti.

Reagent and chemicals :

The reagent was prepared following the method previously described[1] and a 2.5% (w/v) solution of it was prepared in double distilled water. The reagent solution was found to decompose on keeping overnight; fresh solutions were therefore prepared before use.

Other chemicals used were either of A.R. quality or properly purified. Standard solutions of other cations were prepared from their chlorides or sulphates and of anions from their sodium or potassium salts; the strengths were determined by standard methods.

10% HCl and 10% sodium acetate solution were used to adjust the *p*H values.

Absorbance curves :

Procedure : 2.5 cc Ti(IV) solution (100 ppm) was taken in a beaker and treated with 10 cc of reagent solution (2.5%). The *p*H of the solution was adjusted between 1.5 and 2.5 by adding in drops of 10% HCl and 10% sodium acetate solutions. It was then transferred into a 25 cc volumetric flask and diluted upto the mark. The optical density of the solution was then measured at the wavelengths of 360 nm to 450 nm against a reagent blank (Fig. 1). From the

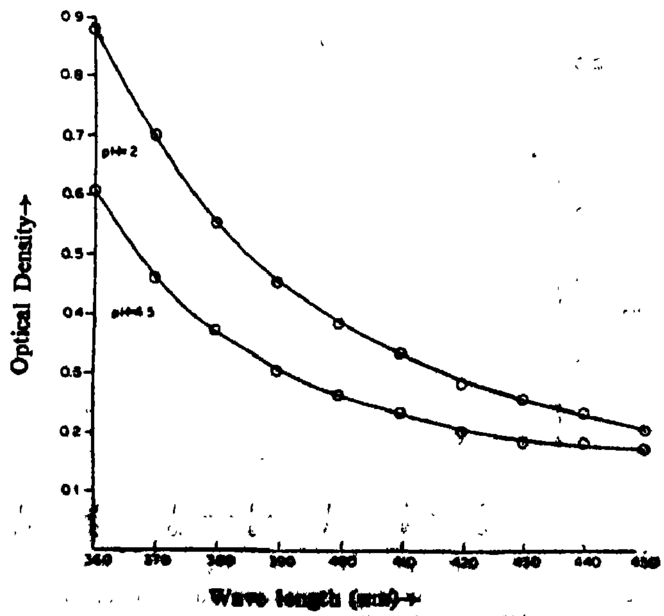


Fig. 1 Absorption Curves of Ti(IV) Complex (Ti=10 ppm)

absorption curves it was observed that the absorbancy gradually increased from 450 nm to 360 nm but without any peak[3,4] and hence in all subsequent studies absorbancy was measured at 410 nm since the reagent showed no absorption in this region.

Effect of pH and time :

The effect of hydrogen ion concentration on the formation of the Ti(IV) complex was studied at 410 nm for 10 ppm of Ti(IV) from *p*H 0.5 to 4.5 (Fig.2). The absorbancy of the Ti(IV) complex remained constant in the *p*H range 1.5 to 2.5. The colour was found to remain stable upto five hours.

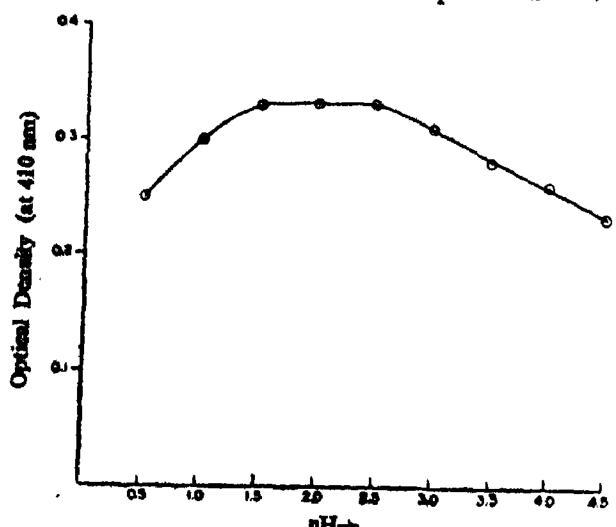


Fig. 2 Effect of *p*H on the Ti(IV) complex (Ti = 10 ppm)

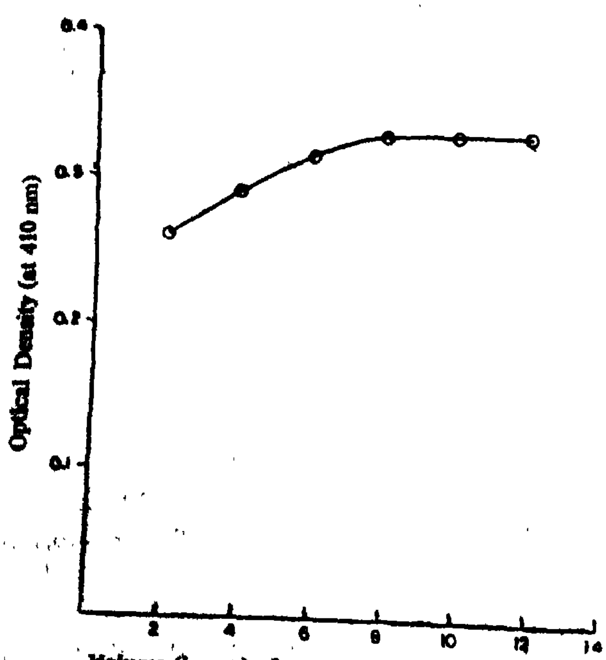


Fig. 3 Effect of reagent concentration on the Ti(IV) complex (Ti = 10 ppm) at *p*H = 2

Effect of reagent :

In this study 10 ppm of Ti(IV) solution were mixed with different amounts of reagent solutions (2.5% w/v) at *p*H = 2 (Fig. 3). It was observed that for the maximal colour development, the amount of the reagent should be as high as 50 times than the theoretical amount showing that the (Ti(IV) complex is highly dissociated in nature and a large excess of the reagent can only influence the equilibrium to get the cent percent of complex formation. Due to this reason Job's method or the mole ratio method could not be applied to determine the composition of the Ti(IV) complex.

Beer's law, optimum range, accuracy and sensitivity :

The yellow Ti(IV) complex was found to obey Beer's law from 4 to 14 ppm of Ti at 410 nm in the *p*H range 1.5-2.5 with a large excess of the reagent (10 cc 2.5%). The optimum range, evaluated from the standard curve[5], was found to be 5 to 14 ppm and the relative error per 1% absolute photometric error[6] was 2.72%. The molecular extinction coefficient was found to be 1.584×10^3. Spectrophotometric sensitivity, calculated according to Sandell[7] was 0.0303 μgm/cm^2.

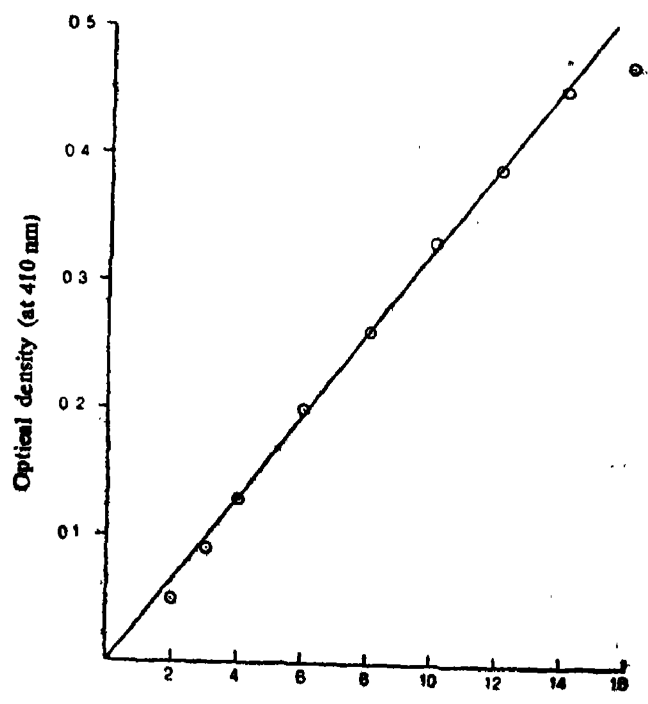


Fig 4 (a) Beer's Law for the Ti(IV) complex at *p*H = 2

Effect of various ions :

To evaluate the tolerance limits for different ions, solutions containing 10 ppm of Ti and varying amounts of other ions were analysed as described under

absorbance studies. Absorbance errors above 0.005 were considered to indicate interference.

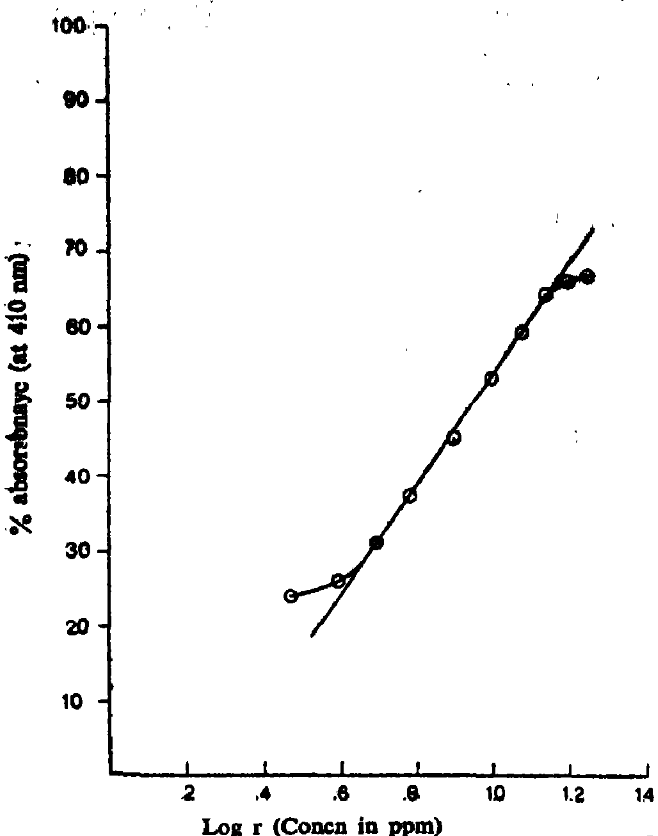


Fig. 4 (b) Standard curve for the Ti(IV) complex at $pH = 2$

In this colour system Ag(I), V(V), Mo(VI), CrO_4^{2-}, PO_4^{3-}, F^- and EDTA interfere. However this system tolerates the presence of the following ions, the tolerance limits of which in ppm are given in parentheses : Mn^{2+}(200), Fe^{2+}(200), Zn^{2+}(200), Cd^{2+}(200), Hg^{2+}(150), Al^{3+}(200), Sn^{2+}(150), Pb^{2+}(150) Bi^{3+}(100), Ce^{4+}(50), Th^{4+}(100), Cr^{3+}(20), Co^{2+}(30), Ni^{2+}(30) and Cu^{2+}(20). WO_4^{2-} can be tolerated in the presence of tartrate and Fe(III) in the presence of ascorbic acid. Howerer Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} do not interfere.

Estimation of Ti(IV) in the presence of Fe(III) and in the presence of Fe(III) and V(V) :

An aliquot solution containing Ti(IV) and Fe(III) or Ti(IV), Fe(III) and V(V) was taken in a 100 cc beaker. 2-3 cc of ascorbic acid (10%) was used to reduce Fe(III) but heated with 2-3 cc of hydroxylamine hydrochloride or hydrazine sulphate (10%) to reduce both Fe(III) and V(V). An excess (10 cc) of the reagent solution (2.5%) was added and the pH was adjusted in the range 1.5 to 2.5 with sodium acetate (10%), HCl(10%) or KOH(10%) as required. The solution was diluted upto 25 cc in a flask and the absorbancy was measured at 410 nm.

The Ti(IV)-Fe(III) system was found to tolerate upto 200 ppm of Fe(III) in the presence of 10 ppm of Ti(IV) with an error below 2.5% but the Ti(IV)-Fe(III)-V(V) system was found to tolerate upto 200 ppm of Fe(III) and 100 ppm of V(V).

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Volumetric Studies in Redox Reactions Part-I. Determination of Mercury(II) by Chloramine-T

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Mercury (II) has been reduced to elemental state with formaldehyde solution in alkaline medium and determined with chloramine-T in a strong hydrochloric acid medium after pretreating with iodine monochloride. The end point is detected as in Andrews titration. The method gives accurate and reproducible results.

THE use of chloramine-T as an oxidising titrant was first proposed by Noll[1]. Rupp[2] used chloramine-T for the determination of antimony (III) and later for the determination of tin(II). Komarowsky[3] *et al* determined several compounds with chloramine-T. In a strong hydrochloric acid medium, in the presence of iodine monochloride, iodide, hydrazine, iron II), arsenic(III), antimony(II), tin(II), mercury (I) and thiocyanate have been titrated with chloramine-T[4]. The present paper describes the use of chloramine-T as a titrant for estimation of mecury (II). It is based on the reduction of mercury (II) to the elemental state with formaldehyde solution in alkaline medium and subsequent determination of the precipitated mercury without separation, with chloramine-T in a strong hydrochloric acid medium, after pretreating with iodine mono chloride. The end point is obtained as in the Andrew titration[5] by the use of carbon tetrachloride.

All the chemicals used were analytical grade BDH Analar or Merck GR. Solution of mercury(II) was prepared by dissolving mercury(II) chloride in distilled water and its strength determined by iodine[6]. Iodine monochloride was prepared from potassium iodide and potassium iodate.

Procedure :

A suitable aliquot of mercury (II) solution was pipetted into a titration flask and 1 ml of formaldehyde solution (40%) followed by 10 ml of 4 N sodium hydroxide was added. The contents of the flask were allowed to stay for about two minutes to complete precipitation of mercury. The contents of the flask were then acidified with hydrochloric acid and to give an acid strength of about 5 N in the solution and 5 ml of iodine monochloride followed by 5 ml of carbontetrachloride added. The reaction mixture was vigorously shaken to dissolve the precipitated mercury and the iodine liberated was titrated with a standard solution of chloramine-T. The end point was taken at the stage where the last trace of violet colour disappeared from organic layer. The results are recorded in the table.

TABLE—1 ESTIMATION OF MERCURY (II) BY CHLORAMINE-T.

Sr. No.	Amount taken (mg.)	Amount Found (mg.)
1	40	39.9
2	60	60 1
3	80	79.9
4	100	99.7
5	120	120.3
6	160	159.9

Formaldehyde precipitates mercury(II) from its solution in alkaline medium :

$$Hg^{2+} + HCHO^- + 3OH^- = Hg + HCOO^- + 2H_2O \quad ...(1)$$

The precipitated mercury is dissolved in iodine monochloride and the equivalent amount of iodine released (eq 2) is titrated with chloramine-T as in Andrews titration :

$$Hg + 2I^+ = Hg^{2+} + I_2 \quad .... \quad (2)$$

$$I_2 + 2[CH_3C_6H_4SO_2NCl^-]Na^+ + 2H^+ = 2I^+ + 2CH_3C_6H_4SO_2NH_2 + 2Na^+ + 2Cl^-$$

Excess of formaldehyde does not interfere in the determination. The method is accurate and utilizes only one standard solution. It is of practical value in the determination of sublimate in which mercury cannot be determined with thiocyanate by Volhard's method.

The interference of acetate, sulphate, phoshate, oxalate, bromide, nitrate, borate, arsenic (V), antimony (V), nickel (II), zinc (II), cobalt (II), lead (II), and cadmium (II) was investigated by adding 80 mg of each ion and it has been found that they do not interfere in the titration. However, manganese (II),

arsenic(III), antimony(III), mercury (I), silver (I) and copper (II) interfere in the determination.

Acknowledgement

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Morpholine-4-Carbodithioate as an Analytical Reagent for Gravimetric Determination of Copper(II)

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Copper (II) has been precipitated quantitatively with morpholine-4-carbodithioate over the pH range 3·0-11·0. The sensitivity of the reagent is 6·0 μg. for copper (II). The separation and determination of copper(II) and nickel(II) has been made in their binary mixtures using ammoniacal solution of EDTA and tartarate. The separation of copper(II) from cobalt(II), Fe(II), Zn(II). Cd(II), Sn(II), Mg(II), Ga(III), In(III), Al(III), Th(IV) and U(VI) is made possible by using an ammoniacal mixture of EDTA and tartarate as the masking agent. Oxo-titanium(IV) and oxo-vanadium(IV) are masked with sodium flouride. The anions, viz. Br^-, F^-, CH_3COO^-, CNS^-, $C_2O_4^{-2}$, PO_4^{-3}, BO_3^{-3}, citrate and tartarate do not interfere in the determination of copper(II), whereas thiosulphate interferes.

Although Bayer and Ott[1] reported morpholine-4-carbodithioate as a possible analytical reagent, the survey of the literature reveals that no analytical work has been carried out on this reagent. In the present communication morpholine-4-carbodithioate has been used as an analytical reagent for the quantitative separation and determination of Cu(II) and Ni(II).

TABLE—1

Sl. No.	Cu(II) mg	Complex mg	Cu(II) Found mg	% Error
1	12·63	77·2	12·64	+0·07
2	18·95	115·6	18·92	−0·16
3	25·26	154·4	25·27	+0·11
4	31·58	192·8	31·56	−0·06
5	50·52	308·2	50·45	−0·13

Experimental

Potassium salt of the reagent was prepared according to the procedure given by Macrotrigiano, *et. al.*[2] The potassium morpholine dithiocarbamate has been prepared by treating morpholine in dry ether with carbon-disulphide and adding potassium hydroxide during four hours, under vigorous stirring. (Molar ratios, morpholine : carbon-disulphide : KOH = 1 : 1 : 1). The crude product was recrystallised from isopropyl-alcohol (melting point of the acid = 175°).

Procedure for the Determination of Copper(II) :

Aliquots (containing 3·5-100 mg.) of the standard solution of the copper (II) were diluted to about 150 ml. with distilled water and the pH was adjusted in between 3·0 and 7·5, by adding appropriate quantities of the acetate buffer solution. A 1% (w/v) solution of the KMDTC in distilled water was then added with constant stirring. A brown precipitate gradually separated out which was digested on a water-bath (60-75°) for about 30-40 minutes. The precipitate was filtered off in a sintered glass crucible (G-4) and washed with distilled water several times. It was then dried at 110-120° for two hours and weighed as $Cu(C_5H_8ONS_2)_2$. The results of the estimations of copper(II) are given in Table I.

Effect of foreign ions :

Determination of copper (II) was carried out in the presence of anions and cations. The anions, *viz.* Br^-, F^-, CNS^-, $C_2O_4^{-2}$, BO_3^{-3}, $S_2O_3^{-2}$, tartarate, citrate and EDTA in three fold excess did not interfere in the determination of copper(II). Ni(II), Co(II), Fe(II), Zn(II). Cd(II), Sn(II), Mg(II), Al(III), In(III), Ga(III), Th(IV) and U(VI) did not interfere in the presence of an ammoniacal mixture of 0·1M tartarate and 0·1M EDTA. Oxo-titanium(IV) and oxo-vanadium(IV) were masked by adding sodium flouride. In the determination of copper(II) in the presence of the above mentioned ions, masking agents were added prior to the addition of the reagent ; the mixture gently heated, and the pH was adjusted to 5·0-7·5 with acetate buffer.

Seapration and Determination of Cu(II) and Ni(II) :

The mixture containing Cu(II) (12·63 mg.) and Ni(II) (12·72 mg.) was taken into a 500 ml. beaker. It was diluted to 200 ml. with distilled water and 10 ml. (0·1 M) of an ammoniacal solution of tartarate and EDTA was added, and the mixture was gently heated for 5 minutes. The pH of the solution was maintained at 5·0-7·0, using acetate buffer. 1% (w/v) reagent (KMDTC) solution was then added with constant stirring. The percipitate was digested at 60-75° for 30 minutes. It was

filtered after an hour in a sintered glass crucible (G-4),[1] washed repeatedly with distilled water, dried at 110-120° for two hours; and weighed as Cu $(C_5H_8ONS_2)_2$.

The filtrate containing Ni(II) was concentrated, and on cooling 10 ml. of concentrated nitric acid (AR) was added, evaporated to dryness, diluted with 10 ml. of distilled water, and again evaporated to dryness. The residue was treated with 150 ml. of distilled water. Any adherent nitric acid was just neutralised with ammonia solution (1 : 1). The 1% (w/v) reagent solution was then added, the yellowish green precipitate obtained was digested at 60-70° for 30 minutes. It was washed with distilled water, dried at 110-120° for two hours, and weighed as $Ni(C_5H_8ONS_2)_2$.

Copper could be determined with an accuracy of ±0.16 per cent; the accuracy for nickel was ±0·5 per cent.

Results and Discussion :

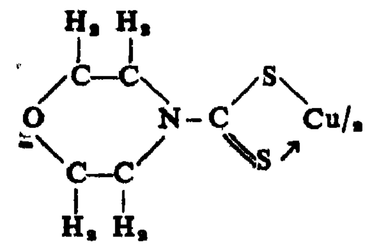
Properties and composition of the Complex : The copper (II) complex is insoluble in ethanol, acetone, benzene, nitrobenzene, ether, ethylacetate, isopropyl alcohol and dioxane. It is partially soluble in chloroform and carbon tetrachloride, and quite soluble in pyridine and aniline. The copper complex was heated at different temperatures in the oven to a constant weight. It was observed that the complex was stable in between 100°-175°±1°. After 175° it starts to decompose slowly.

Digestion of the complex above 85°C yielded low results.

The presence of Ag(I), Pb(II) and Bi(III) interfere in the determination of copper(II).

Structure of the complex :

Based on the elemental analysis and conductometric titrations, the Cu-complex is given the following structure :



Acknowledgements

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Transannular Electronic Interactions of some Cyclobutane Derivatives

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One of the advantages of the molecular orbital theory over early resonance theory is that the former readily accounts for certain electronic interactions between groups which are not conjugated in the classical sence. The purpose of this paper is to describe the syntheses of four cyclobutane derivatives I, II, III and IV and to discuss their unusual ultraviolet absorption spectra which have been determined in ethanol. They all show unusual ultraviolet absorption spectra which have been attributed to transannular electronic interactions. The molecular model constructions of these compounds show the π-orbitals of the transannularly situated chromophores—two carbonyl and two azomethines can come closer to each other cross-wise because of the folded conformation. This is an interesting consequence of the stereochemistry of the four-membered ring. The origin of π-π* transition (K-band) and its assignments are discussed from the standpoint of the transannular electronic interactions (Transannular Conjugation).

BY using cyclohexanecarbonyl chloride (Eastman Kodak Co.) as starting material, Dispiro [5·1·5·1] tetradecane-7,14-dione I and Dispiro [5·1·5·1] tetradecane-7,14-dioxime II were prepared (Fig. 1). Using Isobutyryl chloride (Eastman Kodak Co.) as starting material, 2,2,4,4-tetramethyl-1, 3-cyclo-butanedione III and 2,2,4,4-tetramethyl-1, 3-cyclo-butanedione dioxime IV were synthesized (Fig. 2).

Experimental

Dispiro [5·1·5·1] tetradecane-7, 14-dione[1] *I* :

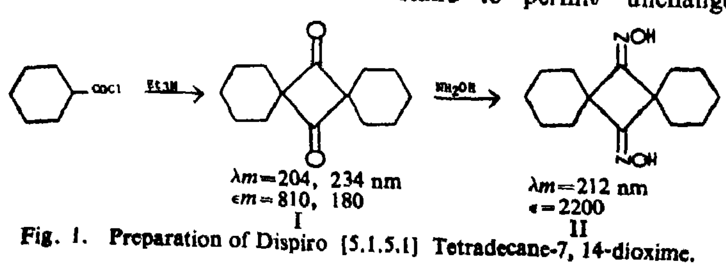
A 500 ml, three-necked, round bottom flask is equipped with a mechanical stirrer, a condenser, a dropping funnel, and a nitrogen inlet. The flask is charged with a solution of cyclohexanecarbonyl chloride (30g, 0·2505 mole) in 250 ml of dry benzene, the system is flushed with nitrogen, and a nitrogen atmosphere is maintained thereafter. In the dropping funnel is placed anhydrous triethylamine (35g, 0.35 mole), which is added to the stirred reaction mixture dropwise (approx. 30 minutes). The mixture is brought to reflux and refluxing is continued (with stirring) 18-20 hours. The cooled solution is then filtered to remove triethylamine hydrochloride, and the filtrate is transferred to a separatory funnel and washed with 200 ml 5% aqueous hydrochloric acid followed by and equal volume of water. The organic solution is dried by sodium sulfate, the benzene is removed (rotary evaporator), and the residue is recrystallized from petroleum ether-ethanol. The weight of the product thus obtained is about 12g (54%), mp 161-162°. The ultraviolet absorption spectra show $\lambda m = 204$ nm with $\varepsilon m = 810$ and $\lambda m = 234$ nm with $\epsilon m = 180$ in 95% ethanol (Fig. 1).

2,2,4,4-Tetramethyl-1, 3-Cyclodecanedione[1] *III* :

Similarly using the above procedure, 2,2,4,4-tetramethyl-1,3-cyclo-butanedione was prepared by using isobutyryl chloride as the starting material. The melting point of the compound is 113-114° (Cf 113-115°). The ultraviolet absorption spectra show $\lambda m = 204$ nm with $\varepsilon m = 145$ and $\lambda m = 226$ nm with $\varepsilon m = 120$ in 95% ethanol (Fig. 2).

Dispiro [5·1·5·1] tetradecane-7, 14-dioxime[2] *II* :

Dispiro [5·1·5·1] tetradecane-7, 14-dione (5g) was treated with 10g of hydroxylamine hydrochloride, 20g of potassium hydroxide, and 80 ml of 95% ethanol. The mixture was heated under reflux for 24 hours and poured into 500 ml of water. The suspension was stirred and allowed to stand to permit unchanged ketone to separate.



$\lambda m = 204$, 234 nm
$\epsilon m = 810$, 180
I

$\lambda m = 212$ nm
$\epsilon = 2200$
II

Fig. 1. Preparation of Dispiro [5.1.5.1] Tetradecane-7, 14-dioxime.

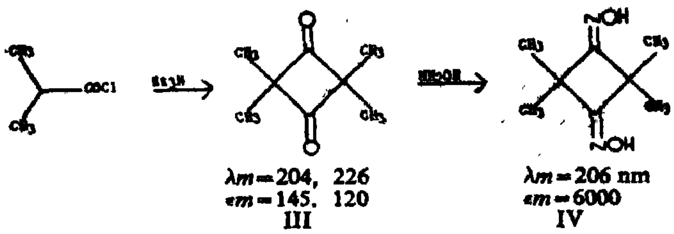


Fig. 2. Preparation of 2,2,4,4-tetramethyl-1, 3-cyclobutanedione dioxime

The solution filtered, acidified with hydrochloric acid and allowed to stand to permit the oxime to crystallize. The product was recrystallized from ethanol or an ethanol-water mixture. The yield was 80%. The melting point of the oxime II is 235°. The infrared absorption shows the right frequency for the oxime group. The ultraviolet absorption spectrum shows $\lambda m=212$ nm with $\epsilon m=2200$ in 95% ethanol (Fig. 1). The elemental analysis, calculated for $C_{14}N_2O_2H_{22}$: C, 67·20% ; H, 8·80% ; N, 11·20% ; Found C, 67.25% ; H, 8·78% ; N, 11·15%.

2,2,4,4-Tetramethyl-1,3-Cyclobutanedione dioxime[2] *IV* :

Similarly using the above procedure, 2,2,4,4-tetramethyl-1,3-cyclobutanedione dioxime was prepared by using 2,2,4,4-tetramethyl-1,3-cyclobutanedione as the starting material. The yield of the compound IV was 85%. The melting point of the oxime IV is 269-270° and is uncorrected. The infrared absorption shows the right frequency for the oxime group. The ultraviolet absorption spectrum shows $\lambda m=206$ nm with $\epsilon m=6000$ in 95% ethanol (Fig. 2). The elemental analysis, calculated for $C_8N_2O_2H_{14}$: C, 56·47% ; H, 8·24 ; N, 16·47% ; Found : C, 56·55% ; H, 8·34% ; N, 16·35%.

Discussion

Cyclobutane Conformation :

Cyclobutane exists in planar and nonplanar conformations. Thermodynamic and spectroscopic studies show the cyclobutane and many of its derivatives exist predominantly in a "butterfly" conformation or folded conformation[3]. The dihedral angle between the two wings of the bent ring is about 25° deviated from the planarity. This folding increases the angle strain of cyclobutane from 90° to 88°, but allows for a greater relief of torsional strain[4] (Fig. 3). There are different folded forms of cyclobutane—a mixture of rapidly oscillating nonplanary conformers. At room temperature, thermal energy causes these forms to be interconverted rapidly[4] (Fig. 4).

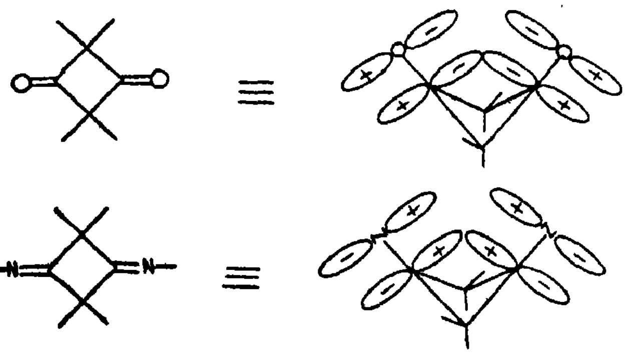


Fig. 3 π-Orbitals Cross-Wise Interaction

In planar form of cyclobutane and its derivatives all the CH_2 groups are in eclipsed conformation. Cyclobutane has more eclipsed C-H nonbonded repulsions, due to this, to reach a more stable level, the planar ring folds slightly and vibrates through the plane[5] (Fig. 4). The folding of the ring (to about 150-160° from the planar 180°) relieves the eclipsing by allowing an approach to a staggered conformation of the C-H bonds around the ring[5].

In nonplanar cyclobutane conformation, the substituents are probably most favorably located in what might be called the less hindered, "Quasi-equatorial positions[6]." The energy of eclipsing the hydrogens in cyclobutane is sufficient to cause the ring to be nonplanar[3]. The cyclobutane ring is most likely to be nonplanar. The nonplanar structure is the most stable.

Transannular Interactions :

The visible and ultraviolet absorption spectra of Dispiro [5·1·5·1] tetradecane-7,14-dione I, Dispiro [5·1·5·1] tetradecane-7,14-dioxime II, 2,2,4,4-tetramethyl-1,3-cyclobutanedione III and 2,2,4,4-tetramethyl-1,3-cyclobutanedione Dioxime IV have been measured in ethanol, and the compounds exhibit an unusual absorption bands. Dispiro [5·1·5·1] tetradecane-7, 14-dione exhibits an unusual absorption band at 204 nm with a molar absorptivity of 810 liter mole^{-1} cm^{-1} ; dispiro [5·1·5·1] tetradecane-7, 14-dioxime shows band at 212 nm with a molar absorptivity of 2200 liter mole^{-1} cm^{-1} ; 2,2,4,4-tetramethyl-1,3-cyclobutanedione shows band at 204 nm with a molar absorptivity of 145 liter mole^{-1} cm^{-1} ; and 2,2,4,4-tetramethyl-1, 3-cyclobutanedione dioxime shows band at 206 nm with a molar absorptivity of 6000 liter mole^{-1} cm^{-1}. These unusual bands have been attributed to transannular electronic interactions.

Similar bands have been observed in the spectra of other related cyclobutane derivatives containing noconjugated chromophores across the ring and have been attributed to transannular electronic interaction[7], (Fig. 5).

Mechanism of Interaction :

These four compounds I, II, III and IV are cyclobutane derivatives. These compounds were chosen because of the favorable geometry for such interactions of the four-membered ring with diametrically opposed two similar functional groups. The folding of four-membered ring brings the

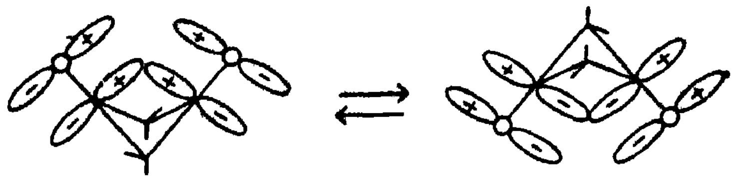
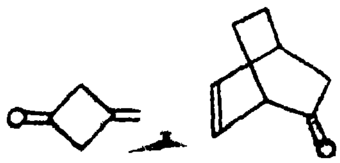


Fig. 4. Cyclobutane Derivative Rapid Transformations.

nonconjugated two >C=O chromophores closer to each other cross-wise in the compounds I and III. Similarly the folding of the cyclobutane ring brings



λm = 214 nm, 284 nm
εm = 1500, 30
V

λm = 202 nm, 290 nm
εm = 3000, 110
VI

Fig. 5. Transannular Interactions in Related Compounds.

the transannular two >C=N—azomethine chromophores closer to each other cross-wise in the compounds II and IV. This permits the orientation of the π-orbitals of two C=O chromophores of I and III and two >C=N— chromophores of II and IV to come closer to each other in cross-wise manner and thus permit an effective overlap interaction of the tπ-orbitals (Fig. 3).

Such an orbital overlap gives rise to bonding and antibonding π-molecular orbitals which encompass both the chromophores. The band can then be assigned to $\pi\text{-}\pi^*$ transition (K-band). This K-band results from $\pi\text{-}\pi^*$ transition and are characterized by high absorptivity.

Transannular Interactions in Other Related Compounds[7] :

A number of examples are listed in Table 1 where comparisons are made with similar transannular electronic interactions of nonconjugated compounds (Table 1).

There are cases where the C=O and C=C are nonconjugated in the classical sence but where

TABLE 1 COMPARISON OF SPECTRAL DATA FOR CYCLOBUTANE DERIVATIVES.

Compound	*Solvent*	*λm, nm*	*εm*
Dispiro [5.1.5.1] tetradecane-7,14-dione I	Ethanol	204	810
Dispiro [5.1.5.1] tetradecane-7,14-dioxime II	Ethanol	212	2200
2, 2, 4, 4-Tetramethyl-1, 3-cyclobutanedione III	Ethanol	204	145
2, 2, 4, 4-Tetramethyl-1, 3-Cyclobutanedione dioxime IV	Ethanol	206	6000
3-Methylenecyclobutanone[7] V	Ethanol	214	1500
Bicylo [2.2.2] 5-Octen-2-one[7] VI	–	202	3000

interaction does occur to produce an absorption band[7]. The structures where this occurs, the C=O and C=C groups are oriented so that there can be effective overlap of the π-orbitals[7]. For example, 3-methylenecyclobutanone V shows a moderately strong band near 214 nm with a molar absorptivity of 1500 liter $mole^{-1}$ cm^{-1}. Compound VI shows band near 202 nm with a molar absorptivity of 3000 liter $mole^{-1}$ cm^{-1} (Fig. 5).

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Reaction Rates and Mechanisms in Aqueous-Organic Solvents : I-Water-Dioxane System

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A new correlation between reaction rate and mechanism and medium effects in aqueous-organic solvents was proposed. This correlation was derived quantitatively and was supported by the data shown for different reactions in water-dioxane mixtures. Such a correlation has the advantage that it does not involve any acidity function but does however need precise measurements of the water ionisation constant over the full aqueous-organic solvent composition range at the different temperatures. Mechanisms of acid- and base-catalysed reactions were discussed on the basis of solvation characteristics and activity coefficient behaviour of the particular reacting substrate and transition state in the reaction. A distinction between the different groups of these reactions was also reviewed and was applied for reactions in water-dioxane mixtures.

HAMMETT acidity function appears to be well established for aqueous solutions in both acidic as well as basic media. The original concept tath, providing the relevant ioniation occurred, a particular acidity function was independent of the class of indicator used to measure it, has been proved incorrect[1-4]. This makes the use of acidity functions as a criterion of mechanism reliant upon nkowledge of the variation of reaction rate with acidity function for reactions of known mechanism. In particular to assign a mechanism to a given reaction, a series of reactions conforming to the possible alternatives must previously have been studied. Less extensive studies and spectrophotometric measurements of acidity function have already been reported for solutions of mixed solvents. For a fixed concentration of hydrochloric acid over the full aqueous organic solvent (ethanol, acetone or dioxane) composition range there[5-8] was a minimum acidity at a particular solvent composition. H_0 scales have also been recorded for $HClO_4$ [9,10] and HCl and H_2SO_4[11,12] in 40-60 and 60-40 water-dioxane mixtures. Comparison of H_0 for H_2SO_4 in 5-95% dioxane-water[13] with that for H_2SO_4 in water showed that the former was greater for acid concentration up to 6 mole/liter. The ionisation of various uncharged acids and bases in ethanol-and dioxane-water mixtures was investigated[5] by a differential potentiometric method. An interesting comparison of acidity measures for ethanol-water mixtures with particular emphasis on the acidity functions H_0 and H_- was reported[14]. The basicity of aqueous alcohols or dioxane containing base has also been measured[15]. In all the aqueous alcohols studied a regular change in basicity was observed. This is quite unlike the previous data for H_0[5,8]. Qualitatively the situation can be explained as a gradual and continuous change in the effective autoprotolysis constant and in the difference in energy of the proton relative to water.

Very few studies have been reported in which reaction rates are correlated with acidity function in aqueous-organic solvents. Log k_1 is approximately a linear function of H_0 for the HCl catalysed rearrangements of phenylpropenyl- and ethynylpropenyl carbinol[8]. The rates of the acid catalysed hydrolysis of methyl toluene-4-sulphinate in aqueous dioxane increased faster than acid but slower than h_0 with changing acid concentration or solvent composition[16].

However, in aqueous-organic solvents, acidity function and its correlations with reaction rates and mechanisms have not been sufficiently studied, both experimentally and theoretically. The aim of the present investigation is to present a new correlation between reaction rates and medium effects in these media. This correlation will be derived quantitatively and tested for the different acid- and base-catalysed reactions. Mechanisms of these reactions will also be discussed on the basis of solvation phenomena. Experimental data in the literature[8,16-20] supporting the conclusions will be presented.

Theoretical

What I wish to present, now, is a correlation of reaction rate and mechanism with medium effects for acid-and base-catalysed reactions in aqueous-organic solvents. This is based on my discovery that, for most such reactions[8,16-20], plots of $(\log k_{obs} - pK_W)$ *versus* $\log C_W$, at constant temperature, are generally very nicelylinear. Examples are given in Fig.1. Equation (1) is therefore applicable in which C_W is the concentration and K_W is the ionisation constant of the water which is present as a component of the solvent system and k_{obs} is the observed rate constant.

$$\log k_{obs} - pK_W = n \log C_W + \text{constant} \quad (1)$$

The slope of any of these straight lines constitutes a parameter, called n, which describes the manner in which the particular reaction responds to acid or base catalysis. A value for n could be looked upon as the change in number of solvated water molecules in passing from reactants to the transition state in the rate determining step. This is an extreme interpretation.

By analogy with Bunnett's observations[21] for acid solution it is probable that n is a function of both the mechanism of the reaction and the chemical structure of the reacting substrate. This probability cannot be assessed until many more experimental results are available for consideration. It is well known that the rates of acid- and base-catalysed reactions depend on the acid and base concentration. But they do not all depend in the same way. It is worth noting that studies with mixed solvents permit two rather different sorts of variation of acidity and as a result two rather different kinds of correlation of rate with medium effects. One type of variation is that obtained by changing the concentration of a strong acid (or base) in a solvent of fixed composition[6,22]. This type of variation minimises the change in the properties of the medium other than acidity. Consequently such solutions should be particularly favorable for investigating mechanistic implications of correlations of rate with acidity. Acidity function scales for changing acid concentration in a fixed solvent composition will then have similar significance and usefulness as the corresponding scales for aqueous solutions providing ion association is negligible. However, in some cases this is not true, particularly for solvents of low dielectric constant where ion association becomes significant.

Another type of variation of acidity for mixed solvents is that given by changes in the solvent for fixed concentration of acid (or base) solute[7,8,17-19]. This kind of variation will usually involve large changes in the properties of the medium. As a result it should not be surprising that correlations between rate and H_0 are not exact and are in fact rather poor[6], particularly for the solvents of lowest dielectric constant. Acidity functions for a fixed acid (or base) concentration in a series of aqueous solutions with varying solvent composition apparently have less generality and usefulness and therefore less significance. Correlations of reaction rates with acidity function scales are also not as satisfactory as for solutions in which the catalysing acid (or base) concentration is varied in a fixed solvent composition. Even so, these results are of considerable interest in view of the author's hypothesis which predicts linear correlation between ($\log k_{obs} - pK_W$) and $\log C_W$ in aqueous-organic solvents. Very nice straight lines were obtained for water-dioxane mixtures[8,16-20] in both lower as well as higher dielectric constant media (Fig. 1).

On the other hand, it is evident[23] that the ionisation constant of water, K_W, varies with progressive addition of organic solvents. Thus while $K_W = 1.008 \times 10^{-14}$ in pure water, it takes the value 23.99×10^{-16}, 18.09×10^{-17} and 13.95×10^{-19} in 20, 45 and 70% dioxane-mixtures by weight at 25°. This means that K_W should be considered as a function of solvent composition and is not constant as considered before[1,4,24,26].

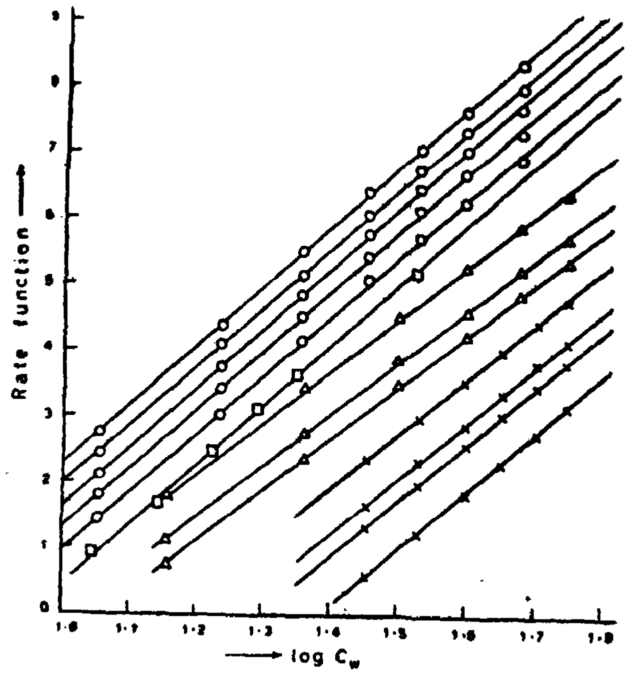


Fig. 1. Test of equation (I) for the differant reactions
□ Ref 16, △ Ref 17, × Ref 18, O Ref 19

Since the velocity constants and mechanisms are quite firmly established for the reactions under consideration[8,16-20] the observed proportionality between ($\log k_{obs} - pK_W$) and $\log C_W$ lends strong support to the validity of the author's hypothesis. It should be noted that this new approach is applicable only to reactions in aqueous-organic solvents, and not to reactions in pure aqueous acidic or basic solutions. It is therefore of interest to evaluate what information on the mechanism can be obtained from this relationship in more general cases.

Medium Function and Reaction Rates and Mechanisms

Zucker and Hammett hypothesis[26] stated that reactions whose rate follows the appropriate indicator acidity function operate through a unimolecular conversion of the active species, while reactions whose rate tends to follow the stoichiometric acidity of the solution operate by a bimolecular reaction of the active species with solvent water. Thus the use of the Zucker–Hammtet treatment as a criterion of mechanism is limited particularly when the dependence of rate with acidity falls somewhere between the two possibilities allowed by the theory.

Bunnett[21] noted that for many reactions ($\log k_1 + H_0$) was a linear or approximately linear function of $\log a_w$ where w is the slope of the graph. Bunnett[31] has suggested that the value of w for an acid-catalysed reaction may provide a useful criterion for the mechanism of that reaction. However, for certain reactions the plots appropriate to the determination of w were not linear. In these cases, one of other three equations is obeyed and enables the deduction of a parameter w^* which is a useful criterion of reaction mechanism. However it is unwise[4] to take the Bunnett criteria, or generally the acidity function concept, alone as the only evidence for the mechanism of a particular reaction. Other independent confirmatory evidence is desirable.

The acidity function dependence of reation rates will probably not only depend on the mechanism of the reaction and the solvation of the hydrogen or the hydroxide ion but also on the solvation characteristics and activity coefficient behaviour of the particular reacting substrate and transition state in the reaction.

I-*Acid-catalysed reactions*

The indicator acidity functions, treated originally as empirical concepts, have been rationalised by Bascombe and Bell[27,28] who showed that the high acidities encountered in concentrated acid solutions are primarily due to the strong hydration of the proton in these solutions. The existence of protons in a tetrahydrated form $(H_9O_4)^+$ has been suggested by many investigators using a variety of experimental techniques[29]. When the solvation is taken into account, the relevant proton transfer equilibrium may be written as

$$B(H_2O)_p + H(H_2O)_q^+ \rightleftharpoons BH(H_2O)_r^+ + hH_2O \quad (2)$$

where B is an electrically neutral week base ; p, q and r are the hydration numbers of B, H_a^+ and BH^+ respectively and $h = (p + q - r)$.

Gluecka[30] found that any anion larger than chloride ion may be considered as nonhydrated in the thermodynamic sense. As B and BH^+ are generally relatively large organic molecules, their solvation requirements may be neglected. However it is probably better to consider h in equation (2) as the difference in the solvation number.

Considering the solvation requirements, the main types of acid-catalysed reactions[4,6] in aqueous-organic solvents may be summarised from the author's point of view as follows :

1—The A—1 mechanism for the hydrolysis of an organic solute S may be written as

(i) $S(H_2O)_p^+ + H(H_2O)q^+ \rightleftharpoons SH(H_2O)_r^+ + hH_2O$ (fast, pre-equilibrium)

(ii) $SH(H_2O)_r^+ \rightarrow X^+$ (slow)

(iii) $X^+ + H_2O \longrightarrow$ products (fast)

The rate determining step is the unimolecular decomposition of the protonated hydrated substrate to an intermediate which rapidly reacts with water to give the reaction products, The rate of loss of the sum of the equilibrium concentrations of S and SH^+ is given by the equation

$$-\frac{d(C_s + C_{SH^+})}{dt} = k_1 C_{SH^+} \frac{f_{SH^+}}{f^*} \quad (3)$$

where k_1 is the rate constant for the slow step and f^* is the activity coefficient of the transition state for that step. The experimental (observed) first order rate constant k_{obs} is defined by the equation

$$k_{obs} = -\left[\frac{1}{C_s + C_{SH}^+}\right] \frac{d(C_s + C_{SH}^+)}{dt} \quad (4)$$

combination of equations (3) and (4) with the expression for the acid ionisation constant K_{SH^+} of hydrated SH^+ leads to

$$k_{obs} = \left(\frac{C_s}{C_s + C_{SH^+}}\right) \frac{k_1 C_H^+ \quad f_H^+ \; f_s}{K_{SH}^+ \; C_w^h \; f_w^h f^+} \quad (5)$$

In acid solutions the variation of the rate of an acid-catalysed reaction with changing solvent composition depends on the reaction mechanism and the relative values of the rate constants in each step of the mechanism. However the activity coefficient behaviour of the reactants and the transition state also makes a significant contribution to the variation of rate with solvent composition (medium effect). This activity coefficient behaviour is intimately connected with the solvation requirements of the reactants and transition state.

It was assumed[29] that the ratio of the activity coefficients is equal to unity. This might be justified in view of the theories of Stokes and Robinson[31,32] and of Glueckauf[29,30] concerning the thermodynamic behaviour of concentrated electrolytic solutions. Stockes and Robinson show that when hydration is taken into account, most of the deviation from ideality disappears, and the remaining deviations can be accounted for by the electrostatic interaction. The ion size parameter of KOH and NaOH is not very different from most other salts ; consequently the electrostatic contribution to the activity coefficient ratio will be negligible[29].

However the author assumes that the activity coefficient ratio on the right-hand side of equation (5) varies with changes in the medium in essentially the same way as, K_w, the water ionisation constant. Such an assumption is a priori reasonable,

since K_w, is a function of solvent composition as mentioned above. Therefore, it may be assumed that this activity coefficient term in equation (5) would vary inversely with water ionisation constant according to equation (6) which leads to equation (7) for the observed rate constant (a_1 is a constant). This assumption may now be expressed as :

$$\frac{f_{H^+}}{f_w^h}\frac{f_S}{f^*} \propto \frac{1}{K_w} \quad \text{or} \quad \frac{f_{H^+}}{f_w^h}\frac{f_S}{f^*} = \frac{a_1}{K_w} \tag{6}$$

and then,

$$k_{obs} = \left[\frac{C_S}{C_S + C_{SH^+}}\right]\frac{a_1k_1}{K_{SH^+}}\frac{C_{H^+}}{C_w^h}\frac{1}{K_w} \tag{7}$$

Three situations now arise and depend upon the relative values of C_S and C_{SH^+}.

(a) If $C_{SH^+} << C_S$, the equilibrium (i) lies practically entirely on the left-hand side, equation (7) becomes

$$k_{obs} = \frac{a_1k_1}{K_{SH^+}}\frac{C_{H^+}}{C_w^h}\frac{1}{K_w} \tag{8}$$

which on taking logarithms is equivalent to

$$\log k_{obs} - pK_w = \log C_{H^+} - h\log C_w + \text{constant} \tag{9}$$

It is clear that equation (9), for a fixed acid concentration, is a quantitative derivation of the emperical relationship expressed by equation (1). Therefore, it may be concluded that the activity coefficient ratio should be dependent on the reciprocal of the water ionisation constant as given by equation (6). Equation (9), or the emperical equation (1), has the advantage that it does not involve any acidity function but does however need precise measurements of the water ionisation constant, K_w, over the full aqueous organic solvent composition range at the different temperatures.

(b) If $C_S \simeq C_{SH^+}$ in the pre-equilibrium mixture, their concentrations are related *via* K_{SH^+}. Hence substitution for C_{SH^+} in equation (7) leads to

$$k_{obs} = \frac{a_1k_1}{K_{SH^+}}\left[1 + \frac{a'_1 C_{H^+}}{K_{SH^+} C_w^h K_w}\right]^{-1} \frac{C_{H^+}}{C_w^h}\frac{1}{K_w} \tag{10}$$

which, on rearrangement and taking the logarithms, gives

$$\log k_{obs} = \log(a_1k_1) - \log\left[\frac{K_{SH^+} C_w^h K_w}{C_{H^+}} + a'_1\right] \tag{11}$$

(c) Finally if $C_S << C_{SH^+}$, then all the added substrate S is protonated in the pre-equilibrium step, equation (10) therefore reduces to

$$k_{obs} = \frac{a_1}{a'_1}k_1 \tag{12}$$

then the observed reaction rate will be independent of acid concentration.

2-The A-2 mechanism for acid-catalysed hydrolysis has a bimolecular rate determining step and may be represented by,

(i) $S(H_2O)_p + H(H_2O)_q^+ \rightleftharpoons SH(H_2O)_r^+ + hH_2O$, (fast, pre-equilibrium)

(ii) $SH(H_2O)_r^+ + Y \xrightarrow{k_2}$ products (slow)

The rate of loss of the sum of the equilibrium concentrations of S and SH^+ is given by the equation

$$-\frac{d(C_S + C_{SH^+})}{dt} = k_2 C_{SH^+} C_Y \frac{f_{SH^+} f_Y}{f^*} \tag{13}$$

The experimental second order rate constant k_{obs} is defined by the equation,

$$k_{obs} = -\frac{1}{(C_S + C_{SH^+})(C_Y)}\frac{d(C_S + C_{SH^+})}{dt} \tag{14}$$

$$k_{obs} = \frac{C_S}{C_S + C_{SH^+}}\frac{k_2}{K_{SH^+}}\frac{C_{H^+}}{C_w^h}\frac{f_{H^+} f_S f_Y}{f_w^h f^*} \tag{15}$$

Following the assumption expressed as equation (6) one may obtain,

$$\frac{f_{H^+} f_S f_Y}{f_w^h f^*} = \frac{a_2}{K_w} \tag{16}$$

and
$$k_{obs} = \left[\frac{C_S}{C_S + C_{SH^+}}\right]\frac{a_2k_2}{K_{SH^+}}\frac{C_{H^+}}{C_w^h}\frac{1}{K_w} \tag{17}$$

for the A-2 mechanism. Equations (17) and (7) are identicals and lead to similar results. As the linear dependence of ($\log k_{obs} - pK_w$) on $\log C_w$ is vrey nicely represented, the proposed assumption expressed as equation (6), or (16), seems justified.

If Y is a water molecule and if $C_{SH^+} << C_s$, then in aqueous solutions the rate-determining reaction will show first-order kinetic as will the overall reaction at constant acidity, the rate constant k_{obs} will satisfy the equation,

$$k_{obs} = \frac{k'_1}{K_{SH^+}} \frac{C_{H^+}}{C_w^{h-1}} \frac{f_{H^+}\ f_S}{f_w^{h-1}\ f^*_c}, \quad (18)$$

$$\text{or,}\quad k_{obs} = \frac{a'_1 k'_1}{K_{SH^+}} \frac{C_{H^+}}{C_w^{h-1}} \frac{1}{K_w}, \quad (19)$$

or, taking logarithms,

$$\log k_{obs} - pK_w = \log C_{H^+} - (h-1)\log C_w + \text{constant.} \quad (20)$$

This equation shows a linear dependence of ($\log k_{obs} - pK_w$) on $\log C_w$, a relation which was predicted emperically (equation 1). In this case the slope is equal to (h—1) and not to —h as given by the previous cases.

Both of the foregoing A—1 and A—2 mechanisms presuppose a rapid equilibrium between the hydrated reactant S and its hydrated conjugate acid SH^+. For the particular case of catalysis by a strong acid, evidence for such an equilibrium is afforded by an increase in the reaction rate when D_2O is substituted for H_2O as the reaction medium[6].

3—A further mechanistic possibility which is relevant to the present discussion is that in which protonation of the hydrated substrate molecule is the rate-determining step in the reaction

$$\text{(i)}\quad S(H_2O)_p + H(H_2O)_q^+ \longrightarrow SH(H_2O)_r^+ + hH_2O \quad \text{(slow)}$$

$$\text{(ii)}\quad SH(H_2O)_r^+ + Y \longrightarrow \text{products} \quad \text{(fast)}$$

The rate equation will have the form :

$$\text{Rate} = -\frac{dC_s}{dt} = kC_s C_{H^+} \frac{f_s\ f_{H^+}}{f^*} \quad (21)$$

where k is the rate constant for the protonation step. The value of k would of course be different for catalysis by some other acid than the solvated proton. The observed rate constant k_{obs} is given by[4]

$$k_{obs} = -\frac{1}{C_s}\frac{dC_s}{dt} = kC_{H^+} \frac{f_s\ f_{H^+}}{f^*}$$

$$k_{obs} = a'_s\, k\, C_{H^+} / K_w \quad (23)$$

taking logarithms,

$$\log k_{obs} - pK_w = \log C_{H^+} + \text{constant} \quad (24)$$

For a fixed acid concentration, $\log k_{obs}$ varies only and directly with pKw. The proposed designation A-S_{E_2} suggests that this is a typical electrophilic substitution reaction. The difference in the hydration number, h, is equal, in this case, to zero. This mechanism, however, differs from others by being independent on $\log C_w$.

II *Base-catalysed reactions*

It is evident[29] that the theory of Bascombe and Bell[27,28] is applicable to concentrated alkaline solutions and leads to the conclusion that three moles of water are associated with each mole of hydroxide ion, which may be formulated as $OH(H_2O)_3^-$. However, following the approach developed by Bell and Bascombe[27,28], it is profitable to consider the change in solvation for the ionisation in aqueous basic solutions of a weak uncharged acid. This may be represented by the equilibrium,

$$HA(H_2O)_{p'} + OH(H_2O)_{q'}^- \rightleftharpoons A(H_2O)_{r'}^- + (h'+1)H_2O, \quad (25)$$

in which p',q' and r' are the hydration numbers of HA, OH^-, and A^- respectively and $h' = (p'+q'-r')$ is the difference in hydration numbers on ionisation. Edward and Wang[35] take account of the fact that the hydroxide ion, because of its small size and localized charge, is almost certainly more heavily hydrated than the usual organic conjugate base A^- with a charge dispersed by resonance.

Taking into consideration the hydration of the hydroxide ion, the main types of base-catalysed reactions[24,33] in aqueous-organic solvents may be discussed from the author's point of view as follows :

1-The hydrated substrate SH is in rapid pre-equilibrium with its hydrated conjugate base S^- which is then converted to the products of the reaction in a unimolecular rate-determining step,

$$\text{i)}\quad SH(H_2O)_{p'} + OH(H_2O)_{q'}^- \rightleftharpoons S(H_2O)_{r'}^- + (h'+1)H_2O \quad \text{(rapid preequilibrium)}$$

$$\text{ii)}\quad S(H_2O)_{r'}^- \longrightarrow \text{products} \quad \text{(slow)}$$

In the following treatment only cases $C_{S^-} << C_{SH}$ will be considered, so that C_{SH} will also represent the total concentration of the substrate. The rate expression is given by

$$-\frac{dC_{SH}}{dt} = k_1 C_{S^-} \frac{f_{S^-}}{f^*} \quad (26)$$

where f^* is the activity coefficient of the transition state. The experimental rate constant, k_{obs}, is given by the equation,

$$k_{obs} = -\frac{1}{C_{SH}}\frac{dC_{SH}}{dt} = k_1 \frac{C_{S^-}}{C_{SH}}\frac{f_{S^-}}{f^*} \quad (27)$$

$$k_{obs} = k_1 K_{SH} \frac{C_{OH^-}}{C_W^{h'+1}} \cdot \frac{f_{SH} f_{OH^-}}{f^* f_W^{h'+1}}. \quad (28)$$

If the assumption, made in the acid-catalysed reactions, also holds in this case, then

$$\frac{f_{SH} f_{OH^-}}{f^* f_W^{h'+1}} = \frac{b_1}{K_W} \quad (29)$$

where b_1 is a constant and

$$\log k_{obs} - pK_W = \log C_{OH^-} - (h'+1)\log C_W + \text{constant} \quad (30)$$

2—The hydrated substrate SH is in rapid pre-equilibrium with its hydrated conjugate base S^-, as in mechanism 1, but S^- is subsequently converted to the products in a bimolecular rate-determining interaction with another reactant Y,

i) $SH(H_2O)_{p'} + OH(H_2O)^-_{q'} \rightleftharpoons S(H_2O)^-_{r'} + (h'+1)\,H_2O$ (rapid pre-equilibrium)

ii) $S(H_2O)^-_{r'} + Y \longrightarrow$ products (slow)

The rate is given by the equation

$$-\frac{dC_{SH}}{dt} = k_2 C_{S^-} C_Y \frac{f_{S^-} f_Y}{f^*} \quad (31)$$

where k_2 is the rate constant for the slow step and f^* is the activity coefficient of the transition state for that step. The experimental rate constant, k_{obs}, is given by

$$k_{obs} = -\frac{1}{C_{SH} C_Y}\frac{dC_{SH}}{dt} = k_2 K_{SH} \frac{C_{OH^-}}{C_W^{h'+1}} \frac{f_{SH} f_Y f_{OH^-}}{f^* f_W^{h'+1}} \quad (32)$$

Similar treatment to that considered in the previous cases, one obtains

$$\frac{f_{SH} f_Y f_{OH^-}}{f^* f_W^{h'+1}} = \frac{b_2}{K_W} \quad (33)$$

and $\log k_{obs} - pK_W = \log C_{OH^-} - (h'+1)\log C_W + \text{constant}$ (34)

Both cases (1) and (2) show a similar linear dependence of ($\log k_{obs} - pK_W$) on $\log C_W$ at a fixed base concentration except for the values of the constants.

A case of special importance occurs when Y is a water molecule, and the reaction is pseudo-first order. Inserting H_2O instead of Y yields,

$$k_{obs} = -\frac{1}{C_{SH}}\frac{dC_{SH}}{dt} = k_1' K_{SH} \frac{C_{OH^-}}{C_W^{h'}} \frac{f_{OH^-} f_{SH}}{f_W^{h'} f^*}, \quad (35)$$

for the experimental rate constant. It follows that,

$$\log k_{obs} - pK_W = \log C_{OH^-} - h'\log C_W + \text{constant}, \quad (36)$$

($\log k_{obs} - pK_W$) of a reaction which proceeds by bimolecular interaction of S^- with a water molecule should be linearly dependent on $\log C_W$ with a slope equal to.—h', the difference in hydration numbers on passing from the reactants to the transition state.

3—An alternative mechanism for base catalysis is that in which the abstraction of a proton rom the hydrated reacting substrate is the slow rate-determining step

i) $SH(H_2O)_{p'} + OH(H_2O)^-_{q'} \longrightarrow S(H_2O)^-_{r'} + (h'+1)H_2O$ (slow)

ii) $S(H_2O)^-_{r'} \longrightarrow$ products (fast)

The rate expression in this case will be

$$-\frac{dC_{SH}}{dt} = k\, C_{SH} C_{OH^-} \frac{f_{SH} f_{OH^-}}{f^*} \quad (37)$$

The observed rate constant, k_{obs}, is given by

$$k_{obs} = -\frac{1}{C_{SH}}\frac{dC_{SH}}{dt} = k\, C_{OH^-} \frac{f_{SH} f_{OH^-}}{f^*} = \frac{b\, k\, C_{OH^-}}{K_W} \quad (38)$$

taking logarithms,

$$\log k_{obs} - pK_W = \log C_{OH^-} + \text{constant} \quad (39)$$

This equation is identical with equation (24) for $A\text{-}S_E2$ mechanism showing the linear dependence of $\log k_{obs}$ on the pK_W for this type of both acid- and base-catalysed reactions. The observed rate constant will therefore behave in the same way in the two cases.

4-A nucleophilic attack on the hydrated substrate by hydrated OH^- ion in the rate determining step,

$S(H_2O)_{p'} + OH(H_2O)^-_{q'} \rightarrow$ products (slow)

the transition state in this case is rather similar to that of proton abstraction by OH^- ion (mechanism 3), the difference being only in the point of attack. The rate expression has consequently the same form as equation (39) and can be derived in the same way.

5-Rapid reversible hydroxide additions precede the rate determining step,

$$S(H_2O)_p + OH(H_2O)_q^- \rightleftharpoons SOH(H_2O)_r^- + h'H_2O, \quad (40)$$

followed by (a) $SOH(H_2O)_r^- \longrightarrow$ products, (slow)

(b) $SOH(H_2O)_r^- + Y \rightarrow$ products, (slow)

or (c) $SOH(H_2O)_r^- + H_2O \rightarrow$ products, (slow)

Mechanisms of this type are prevalent in base-catalysed reactions in which carbonyl groups are involved, e.g., amide and ester hydrolysis. Consideration of the previous argument leads to the following expressions for the observed rate constants

Mechanism (5a), unimolecular breakdown of hydrated SOH^-, giving

$$k_{obs} = -\frac{1}{C_S}\frac{dC_S}{dt} = kK\frac{C_{OH^-}}{C_W^{h'}}\frac{f_{OH^-}f_S}{f_W^{h'}f^*}$$

$$= \text{const.}\frac{C_{OH^-}}{C_W^{h'}}\frac{1}{K_W'} \quad (41)$$

or $\log k_{obs} - pK_W = \log C_{OH^-} - h'\log C_W +$ constant (42)

Mechanism (5b), bimolecular reaction of hydrated SOH^- with a second reactant Y, giving

$$k_{obs} = -\frac{1}{C_S C_Y}\frac{dC_S}{dt} = kK\frac{C_{OH^-}}{C_W^{h'}}\frac{f_{OH^-}f_S f_Y}{f_W^{h'}f^*}$$

$$= \text{const.}\frac{C_{OH^-}}{C_W^{h'}}\frac{1}{K_W}, \quad (43)$$

or $\log k_{obs} - pK_W = \log C_{OH^-} - h'\log C_W +$ constant (44)

Mechanism (5c), a special case where $Y = H_2O$, giving

$$k_{obs} = -\frac{1}{C_S}\frac{dC_S}{dt} = kK\frac{C_{OH^-}}{C_W^{h'-1}}\frac{f_{OH^-}f_S}{f_W^{h'-1}f^*}$$

$$= \text{const.}\frac{C_{OH^-}}{C_W^{h'-1}}\frac{1}{K_W}, \quad (45)$$

or $\log k_{obs} - pK_W = \log C_{OH^-} - (h'-1)\log C_W$ + constant. (46)

where k is the rate constant of the slow step and K is the pseudo-equilibrium constant of equation (40).

Results and Discussion

1 *Water-dioxane system*

A comparative discussion can now be made for the acid- and base-catalysed reactions, in water-dioxane mixtures, in terms of the dependence of the rate function L ($L = \log k_{obs} - pK_W$) on $\log C_W$. The water-dioxane system has often been useful in studies of the effect of solvent on acidic and basic dissociation, partly because it covers such a wide range of dielectric constant. Water ionisation constant values for the different water-dioxane mixtures over the temperature range 25-50° were adopted from Harned and Fallon data[28] by interpolation (up to about 81 wt.% of dioxane) from sufficiently large scale plots. The rate expressions of acid-catalysed reactions, may be devided into three groups

1-The first comprise the A-1 and A-2 mechanisms ($C_{SH^+} \ll C_S$) where the rate of reaction will thus follow the equation (9). An example of a reaction following the A-1 mechanism is the acid-catalysed rearrangement of phenylpropenyl- and ethynylpropenyl-carbinol[8] over the entire range of medium composition. The data are given in Table 1. Least square method was generally used to calculate the slopes of all the straight lines and these are given in Table 7. The acid hydrolysis of benzylacetate[19] is an example of an A-2 mechanism. The data are shown in Fig. 1 and Tables 2 and 7. The hydrolysis of tert.butylacetate in presence of 0·05N HCl in several dioxane-water mixtures (0-90% dioxane by weight) was examined[20]. The reaction mechanism changes from $A_{AL}1$, which predominates in water, to $A_{AC}2$ which prevails in dioxane-rich solvents. However, very good straight lines were obtained and the data are given in Tables 3 and 7.

2-The special case of the A-2 mechanism ($Y = H_2O$) represents the second group where the rate of reaction can be expected to follow the equation (20). Examples are given (Tables 4 and 5) for the acid-hydrolysis of acetamide[17] and methyl-toluene-p-sulphinate[16]. Very good straight lines were obtained (Fig. 1) where the slopes represent the-($h-1$) values (Table 7).

TABLE—1 REARRANGEMENTS OF (I) PHENYLPROPENYL- (IN 0.1*M* HCl) AND (II) ETHYNYLPROPENYL-CARBINOL[8] (IN 1*M* HCl) IN DIOXANE-WATER MIXTURES AT 30°.

Vol.%	20	40	60	70	80
$\log C_W$	1.648	1.523	1.347	1.222	1.046
pKw	14.48	15.36	16.79	17.81	19.32
(I) 21+L	6.847	5.515	3.532	2.280	0.519
(II) 21+L	4.538	3.124	1.278	0.199	-

TABLE—2 ACID HYDROLYSIS OF BENZYLACETATE IN DIOXANE-WATER MIXTURES[19] (IN 0.05*M* HCl)

Wt.%	15.45	30.60	40.71	50.46	60.48	70.21	80.33
log Cw	1.675	1.594	1.528	1.452	1.355	1.235	1.054
				25°			
pKw	14.46	15.04	15.52	16.07	16.87	17.88	19.44
25+L	6.875	6.210	5.681	5.047	4.135	3.012	—
				30°			
pKw	14.30	14.86	15.35	15.96	16.75	17.73	19.28
25+L	7.257	6.640	6.091	5.392	4.498	3.407	1.788
				35°			
pKw	14.15	14.73	15.22	15.81	16.61	17.60	19.15
25+L	7.632	6.972	6.421	5.740	4.820	3.724	2.096
				40°			
pKw	14.00	14.59	15.08	15.66	16.48	17.46	19.02
25+L	7.929	7.273	6.715	6.038	5.126	4.080	2.436
				45°			
pKw	13.84	14.46	14.94	15.52	16.32	17.33	18.88
25+L	8.269	7.573	7.032	6.380	5.479	4.363	2.750

TABLE—3 ACID HYDROLYSIS OF TERT.-BUTYLACETATE IN DIOXAN WATER MIXTURES[20] (IN 0.05*M* HCl)

Wt.%	00.00	15.64	31.57	50.06	69.47	79.47
log Cw	1.745	1.671	1.580	1.443	1.230	1.057
			30°			
pKw	13.83	14.31	14.90	15.93	17.64	19.15
24+L	6.917	6.315	5.360	4.047	1.994	0.316
			40°			
pKw	13.54	14.00	14.63	15.63	17.38	18.89
24+L	7.906	7.240	6.359	5.039	2.819	1.038
			50°			
pKw	13.26	13.73	14.37	15.34	17.12	18.62
24+L	8.665	7.968	7.102	5.797	3.531	1.896

TABLE—4 ACID HYDROLYSIS OF ACETAMIDE IN DIOXANE-WATER MIXTURES[17] (IN 0.1 *M* HCl)

Wt.%	0	15	30	40	60	75
log Cw	1.745	1.676	1.597	1.497	1.360	1.158
			35°			
pKw	13.68	14.13	14.71	15.44	16.57	18.32
20+L	5.335	4.819	4.206	3.461	2.362	0.744
			40°			
pKw	13.54	13.98	14.59	15.29	16.43	18.20
20+L	5.687	5.179	4.557	3.817	2.720	1.094
			50°			
pKw	13.26	13.72	14.30	15.03	16.14	17.92
20+L	6.363	5.846	5.232	4.482	3.409	1.785

TABLE—5 ACID HYDROLYSIS METHYLTOLUENE-*p*-SULPHINATE[16] IN DIOXANE-WATER MIXTURES (IN 0.2 *M* $HClO_4$) AT 25.2°

Vol.%	40	60	65	70	75	80
log Cw	1.523	1.347	1.289	1.222	1.143	1.046
pKw	15.53	16.90	17.40	17.96	18.69	19.47
26+L	5.166	3.628	3.101	2.458	1.683	0.925

3-The last group represents the mechanism 3 where the rate of reaction will follow the equation (24). Unfortunately, no experimental data for a reaction known to proceed by mechanism 3 are available at present.

The rate expressions of base-cataylsed reactions may also be devided into four groups.

1-The first comprises the mechanisms 1 and 2 where the rate of the reaction will follow the equation (30).

2-The second group comprises the special case of mechanism 2 ($Y = H_2O$), and mechanisms 5a and 5b, the rate of reaction can be expected to follow the equation (36).

3-The third group comprises mechanisms 3 and 4 where the rate of reaction can be expected to follow the equation (39).

Here again it is to be regretted that no experimental rate data regarding these mechanisms are available at present.

4-The last group is the mechanism 5c where the rate of reaction can be expected to follow the equation (46). An example is the alkaline hydrolysis of acetamide[18] (Tables 6 and 7). Very good straight lines are also obtained (Fig. 1).

TABLE—6 ALKALINE HYDROLYSIS OF ACETAMIDE IN DIOXANE-WATER MIXTURES[18] (IN 0.1*M* NaOH)

Wt.%	0	10	20	30	40	50
log Cw	1.745	1.700	1.651	1.597	1.531	1.453
			25°			
pKw	14.00	14.29	14.62	15.02	15.49	16.04
18+L	3.137	2.740	2.305	1.807	1.245	0.613
			35°			
pKw	13.68	13.97	14.31	14.71	15.18	15.77
18+L	3.812	3.458	3.027	2.540	1.981	1.324
			40°			
pKw	13.54	13.82	14.16	14.59	15.04	15.63
18+L	4.135	3.792	3.363	2.855	2.339	1.672
			50°			
pKw	13.26	13.55	13.89	14.30	14.77	15.34
18+L	4.786	4.422	4.011	3.526	2.981	2.363

TABLE—7 THE SLOPES OF THE STRAIGHT LINES OBTAINED

Temp. °C	25	30	35	40	45	50
Ref. 8 (I)	-	9.86	-	-	-	-
Ref. 8 (II)	-	10.16	-	-	-	-
Ref. 19	8.78	8.90	8.99	8.90	8.93	-
Ref. 20	-	9.66	-	10.02	-	9.92
Ref. 17	-	-	7.82	7.83	-	7.79
Ref. 16	9.01*	-	-	-	-	-
Ref. 18	8.69	-	9.59	8.50	-	8.37

*25.2°

Consequently, it seems likely that the slope of the straight line, obtained by plotting of the rate function L against log C_W, enables, in principle, a distinction to be made between these different groups of either acid- or base-catalysed reactions.

It would be helpful to make further studies[34] to ascertain the generality of the author's hypothesis. In this case, there is every reason to believe that this hypothesis will be highly useful.

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Deriving Equation to Account for the Effect of Added Electrolytes on the Viscosity of Sols of Colloidal Electrolytes

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An equation has been deduced which can account quantitatively for the variation of the ratio, R, the specific viscosity of the sol containing added electrolyte to that of the original sol without any electrolyte, with the increase in concentration of the added electrolyte. The equation has been found to agree well with the data available in the literature on such systems as sols of agar, gum arabic, casein etc. with added electrolytes containing counter ions of different valency.

THE effect of addition, in small amounts, of strong electrolytes on the specific viscosity of a sol of a colloidal electrolyte of given concentration has been investigated by a number of authors[1-3]. Such investigations have led them to the conclusion that a marked lowering of specific viscosity of the sol of a colloidal electrolyte occurs on addition of a strong electrolyte and that the counter ions and their valency are mainly responsible for the effect produced while the coions have practically no effect.

The aforesaid authors have qualitatively accounted for the observed effect with the help of Smoluchowski's extension of Einstein equation[4] which may be written as follows

$$(\eta_s-\eta_0)/\eta_0=\eta_{sp}=k\phi\left[1+\frac{1}{\eta_0 a^2\lambda}\left(\frac{D\zeta}{2\pi}\right)^2\right] \quad \dots(1)$$

where η_s represents the viscosity of the sol, η_0 that of the dispersion medium, k, a constant which is 2.5 for spherical particles according to Einstein, ϕ, the volume fraction, ξ, the electrokinetic potential and a, the radius of the colloidal particles, D, the dielectric constant and λ the specific conductivity of the system.

When a strong electrolyte, in small quantity, is added to the sol, a, η_0 and D remain constant but λ increases appreciably and ξ diminishes to some extent and hence the specific viscosity η_{sp} diminishes. At a given concentration of the added electrolyte as the valency of the counter ion increases, its capacity to reduce ξ and consequently the specific viscosity increases.

It will be shown in this paper that if R represents the ratio of the specific viscosity of the sol containing an added electrolyte to that of the original sol without any added electrolyte, then the variation of R with the increase in concentration of the added electrolyte can be quantitatively accounted for by an equation deduced from theoretical consideration.

Derivation of the equation

It has been shown by the author[5-7], in previous papers that the variation of specific conductivity of a sol of a colloidal electrolyte with dilution can be represented by the following equation :

$$\lambda=\theta\lambda_s+(1-\theta)\lambda_i \quad \dots \quad \dots \quad (2)$$

where θ is the fraction per unit area of the surface of electrode covered by the diffuse double layers of the colloidal particles and is equal to $C/(K_0+C)$ where C is the concentration of the colloidal electrolyte and K_0, a constant, λ_s is the specific conductivity of the diffuse double layer at the plane of contact with the electrode and λ_i the specific conductivity of the intermicellar solution.

Substituting the values of λ and θ in equation (1) it may be written as follows :

$$\eta_{sp}=k\phi\left[1+\frac{(k_0+c)}{\eta_0 a^2(c\lambda_s+k_0\lambda_i)}\left(\frac{D\zeta}{2\pi}\right)^2\right] \quad \dots(3)$$

Let S be the concentration in milliequivalents per liter of the strong electrolyte added to the sol and let its effect in decreasing ξ and increasing λ_i be represented by $\xi(1-bs)$ and $\lambda_i(1+hs)$

† ξ represents the electro-kinetic potential and λ_i the specific conductivity of intermicellar liquid of the orginal sol before addition of any electrolyle. Ther-fore, each of them has got a fixed value. The assumption of linear variatiou of ξ and λ_i should hold good so long as S is small less than 20 millimoles.

respectively, then equation (3) may be written as follows :

$$\eta_{sp} = k\phi\left[1 + \frac{A\xi^2(1-bs)^2}{c\lambda_s + k_o\lambda_i(1+hs)}\right] \quad \ldots(4)$$

where $A = \left(\frac{D}{2\pi}\right)^2 \frac{(c+k_o)}{\eta_o a^2}$, b and h are constants and S is small less than 20 millimoles per liter.

Denoting the specific viscosity of the sol with added electrolyte and that of the original sol without any added electrolyte by $(\eta_{sp})_s$ and $(\eta_{sp})_o$ respectively, we may by using equations (3) and (4) express their ratio, R as follows :

$$(\eta_{sp})_s : (\eta_{sp})_o = R = \left[1 + \frac{A\xi^2(1-bs)^2}{c\lambda_s + k_o\lambda_i(1+hs)}\right] : \left[1 + \frac{A\xi^2}{c\lambda_s + k_o\lambda_i}\right]$$

$$= \left[\frac{c\lambda_s + k_o\lambda_i(1+hs) + A\xi^2(1-bs)^2}{c\lambda_s + k_o\lambda_i + k_o\lambda_i hs} \times \frac{c\lambda_s + k_o\lambda_i}{c\lambda_s + k_o\lambda_i + A\xi^2}\right]$$

Now neglecting $(bs)^2$ as very small compared to the other terms, putting $B = (C\lambda_s + K_o\lambda_i + A\xi^2)$, and $H = (C\lambda_s + K_o\lambda_i)$ and simplifying the above expression, we may write as follows :

$$R = \left[\frac{B - (2A\xi^2 b - k_o\lambda_i h)s}{B} \times \frac{H}{H + k_o\lambda_i hs}\right]$$

$$= \left[\frac{1 - (2A\xi^2 b - k_o\lambda_i h)s/B}{1 + (k_o\lambda_i hs/H)}\right]$$

$$= \left[1 - \frac{1 + (k_o\lambda_i hs)/H - 1 + (2A\xi^2 b - k_o\lambda_i h)s/B}{\frac{k_o\lambda_i h}{H}\left(\frac{H}{k_o\lambda_i h} + S\right)}\right]$$

$$= \left[1 - \frac{ms}{m_o + s}\right] \quad \ldots(5)$$

where $m = \left[\frac{(A2\xi^2 b - k_o\lambda_i h)/B + (k_o\lambda_i h)/H}{k_o\lambda_i h/H}\right]$ and

$m_o = \frac{H}{k_o\lambda_i h} =$ and all the terms in m and m_o are constants for a given added electrolyte.

In equation (5) S, represents the concentration of the counter ions in milliequivalents per liter. If the concentration is to be expressed in milligram ions per liter then equation (5) should be written as follows :

$$R = \left[1 - \frac{m(s/z)}{(m_o/z) + (s/z)}\right] \quad \ldots(6)$$

where z represents the valency of the counter ions of the added electrolyte and (S/Z) represents its concentration in milligram ions per liter.

It may be pointed out that in deducing equation (5) the radius, *a* has been assumed to remain constant. Therefore, it is not applicable to those cases where addition of an electrolyte changes the radius, *a* of the particle.

Notes on the data recorded in the tables :

Kruyt and Bungenberg de Jong[1] have measured the viscosity of purified agar sols (ash content 2·05%) at 50° in the absence as well as in the presence of electrolytes containing counter ions of different valency. Their data taken from the tables VI and VII of their paper[1] are recorded in the Tables I(a) to I(c). Column 2 of the tables, contains the values of the constants m and m_o in equation (5), column 3 contains the concentrations, S in milliequivalents per liter of the added electrolyte. The concentration, S of the electrolyte solution is so small that its viscosity is practically the same as that of water. In column 4 of the tables η_s and η_o

TABLE—I(a) VISCOSITY DATA OF AGAR SOL AT 50° WITH KCl

Experiment no.	Constants	S milli-equiv/L	η_s/η_o	R Observed	R Calculated
1	$m = 0.309$ $m_o = 1.38$	0	1.704	1.0	1.0
		0.05	1.698	0.992	0.989
		0.1	1.689	0.979	0.980
2	$m = 0.309$ $m_o = 1.38$	0	1.719	1.0	1.0
		1.0	1.617	0.858	0.870
		4.04	1.552	0.768	0.770
		10.1	1.515	0.716	0.728

TABLE—I(b) VISCOSITY OF AGAR SOL AT 50° WITH $BaCl_2$

Experiment no.	Constants	S milli-equiv/L	η_s/η_o	R Observed	R Calculated
1	$m = 0.34$ $m_o = 0.62$	0.0	1.704	1.00	1.00
		0.1	1.669	0.950	0.953
		0.2	1.638	0.906	0.917
		1.0	1.556	0.790	0.790
2	$m = 0.34$ $m_o = 0.62$	0.0	1.719	1.00	1.00
		2.0	1.537	0.747	0.740
		4.12	1.511	0.711	0.705
		8.08	1.492	0.684	0.684
		20.2	1.487	0.677	0.670

TABLE—I(c) VISCOSITY OF AGAR SOL AT 50° WITH $Co(NH_3)_6Cl_3$.

Experiment no.	Constants	S milli-equiv/L	η_s/η_o	R Observed	R Calculated
1	$m = 0.373$ $m_o = 0.274$	0.00	1.704	1.00	1.00
		0.045	1.673	0.956	0.947
		0.150	1.620	0.881	0.868
		0.300	1.571	0.811	0.805
		1.00	1.498	0.707	0.707
2	$m = 0.373$ $m_o = 0.274$	0.00	1.719	1.00	1.00
		1.50	1.499	0.694	0.685
		3.00	1.483	0.672	0.658
		6.00	1.471	0.655	0.643
		12.12	1.458	0.637	0.635
		30.30	1.453	0.630	0.630

represent the viscosity of the sol and water respectively. R in the tables has the same significance as stated already.

The effect of strong electrolytes on the viscosity of positively and negatively charged casein sols has been investigated by Kruyt and Lier[2]. The negatively charged casein sol has been prepared by peptising casein with NaOH. The *p*H of the sol is about 10·5 and further addition of alkali to it lowers its viscosity. The positively charged casein sol has been prepared by peptising casein with HCl and the *p*H of the sol is 2.75. According to the authors[2] the negatively charged casein sol becomes opalescent when it is treated with $Co(NH_3)_6Cl_3$ and the positively charged sol flocculates when it is treated with $K_3Fe(CN)_6$ or $K_4Fe(CN)_6$. Therefore, equation (5) cannot be applied to these cases as the radius, *a* of the particles changes as S varies. The data of Kruyt and Lier[2] are recorded in the Tables 2 and 3. The terms S, η_s, η_o and R have the same significance as stated already.

TABLE—2 VISCOSITY DATA OF NEGATIVELY CHARGED CASEIN SOL AT 50°

Electrolyte used	Constants	S milli-equiv/L	η_s/η_o	R Observed	R Calculated
KCl	m = 0.418	0.0	1.279	1.0	1.0
	m_o = 15.5	1.5	1.267	0.957	0.963
		4.0	1.255	0.914	0.914
		9.0	1.236	0.846	0.846
		15.0	1.226	0.810	0.795
$BaCl_2$	m = 0.735	0.0	1.279	1.0	1.0
	m_o = 12.7	1.5	1.261	0.936	0.946
		4.0	1.230	0.824	0.824
		9.0	1.190	0.682	0.695
		15.0	1.168	0.602	0.602

TABLE—3 VISCOSITY DATA OF POSITIVELY CHARGED CASEIN SOL AT 50°

Electrolyte used	Constants	S milli-equiv/L	η_s/η_o	R Observed	R Calculated
$BaCl_2$	m = 0.345	0.0	1.285	1.0	1.0
	m_o = 5.73	1.5	1.264	0.926	0.928
		3.25	1.248	0.870	0.875
		7.00	1.229	0.804	0.811
		13.00	1.213	0.747	0.761
K_2SO_4	m = 0.45	0.0	1.285	1.0	1.0
	m_o = 1.71	0.75	1.246	0.863	0.863
		1.50	1.225	0.790	0.790
		3.25	1.196	0.688	0.701
		7.00	1.182	0.639	0.639

In the Tables 4(a) to 4(d) are recorded the data of Kruyt and Tendeloo[3] on the viscosity of gum arabic sols collected from the tables V, VII and VIII of their papers. The terms, S, η_s, η_o and R have the same significance as stated already.

The data, with reference to equation (6), are recorded in Table 5. Columns 3 and 4 of the table contain the values of the constants m and (m_o/z). In column 5, (S/Z) represents the concentration in milligram ions per liter and the other terms have the same significance as stated already.

TABLE—4(a) VISCOSITY DATA OF GUM ARABIC SOL AT 25°

Electrolyte used	Constants	S milli-equiv/L	η_s/η_o	R Observed	R Calculated
KCl	m = 0.663	0.00	1.528	1.00	1.00
	m_o = 1.45	0.50	1.438	0.830	0.830
		1.00	1.386	0.731	0.729
		5.00	1.257	0.487	0.486
NaCl	m = 0.663	0.00	1.528	1.00	1.00
	m_o = 1.45	0.50	1.438	0.830	0.830
		1.00	1.385	0.729	0.729
		5.00	1.257	0.487	0.486
LiCl	m = 0.663	0.00	1.528	1.00	1.00
	mc = 1.45	0.50	1.438	0.830	0.830
		1.00	1.386	0.731	0.729
		5.00	1.258	0.490	0.486

TABLE—4(b) VISCOSITY DATA OF GUM ARABIC SOL AT 25°

Electrolyte used	Constants	S milli-equiv/L	η_s/η_o	R Observed	R Calculated
$BaCl_2$	m = 0.745	0.00	1.532	1.00	1.00
	m_o = 0.98	0.5	1.405	0.761	0.748
		1.0	1.330	0.620	0.624
		5.0	1.200	0.376	0.377
$SrCl_2$	m = 0.745	0.00	1.532	1.0	1.0
	m_o = 0.98	0.50	1.405	0.761	0.748
		1.00	1.330	0.620	0.624
		5.00	1.200	0.376	0.377
$MgSO_4$	m = 0.745	0.00	1.532	1.00	1.00
	m_o = 0.98	0.50	1.403	0.758	0.748
		1.00	1.330	0.620	0.624
		5.00	1.201	0.378	0.377

TABLE—4(c) VISCOSITY DATA OF GUM ARABIC SOL AT 25°

Electrolyte used	Constants	S milli-equiv/L	η_s/η_o	R Observed	R Calculated
$La(NO_3)_3$	m = 0.882	0.00	1.543	1.00	1.00
	m_o = 1.25	0.50	1.406	0.748	0.748
		1.00	1.330	0.609	0.608
		5.00	1.157	0.289	0.294
$Co(NH_3)_6Cl_3$	m = 0.882	0.00	1.543	1.00	1.00
	m_o = 1.25	0.50	1.406	0.748	0.748
		1.00	1.323	0.595	0.608
		5.00	1.160	0.295	0.294

TABLE—4(d) VISCOSITY DATA OF GUM ARABIC SOL AT 25°

Electrolyte used	Constants	S milli-equiv/L	η_s/η_o	R Observed	R Calculated
*$Pt(en)_3$	m = 1.03	0.00	1.527	1.00	1.00
$(NO_3)_4$	m_o = 1.46	0.50	1.385	0.730	0.737
		1.00	1.306	0.581	0.582
		2.50	1.193	0.366	0.350
		5.00	1.105	0.192	0.203

* $Pt(En)_3(NO_3)_4$. Here En stands for ethyenediamine

Discussion

In column 6 of the tables 1(a) to 4(d) are recorded the values of R calculated by using equation (5). It will be noticed that the calculated values of R agree well with those observed for the sols referred to in the aforesaid tables. It will also be noticed from the data recorded in the aforesaid tables that the ability of the counter ions, at a given

TABLE—5 VISCOSITY WITH REFERENCE TO EQUATION (6)

Colloid	Electrolyte used	Values of m	Values of m_0/Z	S/Z milligram ions/L.	η^s/η_0	R Observed	R Calculated
Agar sole at 50°C	KCl	0.309	1.38	0.00	1.719	1.00	1.00
	,,	,,	,,	1.00	1.617	0.858	0.870
				4.04	1.552	0.768	0.770
	$BaCl_2$	0.34	0.31	1.00	1.537	0.747	0.740
				4.04	1.492	0.684	0.684
	$Co(NH_3)_6Cl_3$	0.373	0.091	1.00	1.483	0.672	0.658
				4.04	1.458	0.637	0.635
Gum arabic sole at 25°C	KCl	0.663	1.45	0.00	1.528	1.00	1.00
	,,			5.00	1.257	0.487	0.486
	$BaCl_2$	0.745	0.49	0.00	1.532	1.00	1.00
				2.50	1.200	0.376	0.377
	$Co(NH_3)_6Cl_3$	0.882	0.417	0.00	1.543	1.00	1.00
	,,	,,	,,	1.67	1.160	0.295	0.294

increases. In agreement with this observation the concentration, to reduce R increases as their valency value of m in equation (5) increases as the valency of the counter ions increases.

From the data recorded in Table 5 it may be concluded that the constant (m_0/Z) in equation (b) diminishes as the valency of the counter ion increases. It indicates, that the ability of the counter ions to increase the specific conductivity of the intermicellar solution, increases as their valency increases.

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Polymeric Materials in Municipa Waterl Treatment

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The efficiency of cationic, anionic, non-ionic polyelectrolytes as aid to coagulation of colloidal water can be increased by the use of fly ash (< 100 mesh), alum sludge (< 1 hr. aged sample) and activated carbon. Reduction of bacteria in the clarified water is an additional advantage using these polyelectrolytes along with fly-ash/alum sludge/activated carbon in the alum treatment process.

Polylectrolytic behaviour of soil humic and hymatomelanic acids were utilized in this connection for clarification of river water along with alum.

RECENT years have witnessed the introduction of a number of synthetic polyelectrolytes in water treatment process[1]. Natural polymers like humic acid, hymatomelanic acid etc. possess polyelectrolyte character[2,3].

An attempt has been made here to find out whether betterment in respect of coagulation and flocculation of turbid water could be made with the simultaneous use of certain polymeric materials including humic and hymatomelanic acids and fly-ash/alum sludge, activated carbon along with prime coagulant alum.

Materials and Methods

River water samples were collected from a fixed depth of basin (0 to 4 ft) near Palta Water (PWW), Barrackpore throughout the representative seasons of the year and the study continued for two consecutive years i.e. 1971-72 and 1972-73. All the studies were made according to Adhikari et al[4]. The coagulation phenomenon was studied thoroughly in 'Jar Test Apparatus' as prescribed by American Public Health Association[4]. The following conditions in Jar Test were maintained :

Speed	:	30 to 40 RPM
Flocculation Time	:	20 minutes
Settling Time	:	10 minutes

Volume of sample in each jar : 910 ml. sequence of addition : First polymeric material, then alum.

The following polyelectrolytes were used in this study :

(a) *Cationic* : *Polyacrylamide (PAAm)*

Acrylamide was polymerized in aqueous solution at 60° using $K_2S_2O_8$ as initiator and the polymer was precipitated by acetone as non solvent and dried under vacuum.

(b) *Anionic* : *Sodium polyacrylate(SPAA) and sodium carboxymethyl Cellulose (SCMC)*

Polyacrylic acid was prepared by thermal polymerization of acrylic acid using benzoyl peroxide as initiator. Sodium carboxymethyl cellulose was supplied by Chemmet, India.

(c) *Non-ionic*

Polyethylene glycol (PEG) was supplied by Union Carbide. Humic acid and hymatomelanic acid and their respective sodium salts were prepared according to Adhikari et al[4] and Ghosh et al[5].

In actual experiment all the polyelectrolytes were added in a fixed dosage of 0.5 mg per litre of turbid water and for fly-ash, alum-sludge and activated carbon, amounts applied were 500 mg, 250 mg and 100 mg respectively per litre of river water. Humic acid, hymatomelanic acid and their sodium salts were applied at a dosage of 1.5 mg/litre, These dosages were determined from preliminary experiment to get the maximum possible reduction of prime coagulant (with close approximation) with water of turbidity 1000 p.p.m.

Results and Discussion

The average physicochemical characteristics of the Ganges water samples are given elsewhere[5]. The analysis of fly-ash is given in our earlier communications[6]. Activated carbon used was of the following characteristics : 100% through 100 mesh, weight : 22 to 25 mg/100 ml suspendibility : 65%, carbon content : 75% and moisture : 5.5%.

A comparative study of the coagulating characteristics of polycationic (i.e. PAAm) and alum is made in terms of residual turbidity of treated water against the addition of addendas and is shown in Fig. 1(a). The curve for the former is steeper in comparison to the latter and is considered as due to stronger eneshment of polyelectrolytes and clay in

the flocculation phase. Polycationic actually has prevented any carry over[11] of soluble Al_2O_3.

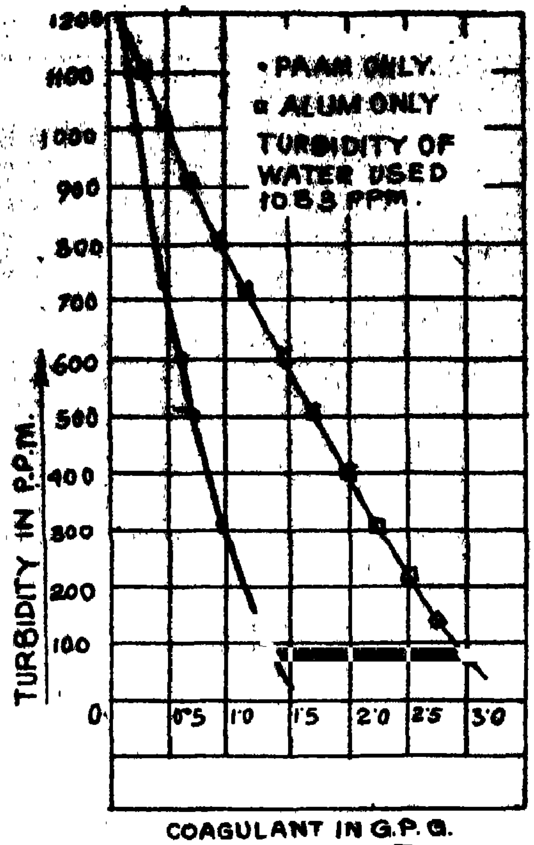


Fig. 1(a)

Table 1 shows the effectiveness in coagulation and floc formation of PAAm, SPAA, SCMC and PEG in presence of ash along with basic alum for limiting coagulation. The following order was observed in terms of extent of diminunition of original alum dosage : SPAA > SCMC > PAAm > PEG. Similar order was noticed when alum sludge and activated carbon were used instead of ash, although activated carbon itself is a good adjunct to flocculation, because of its superior adsorption capacity. The laboratory experimentations with polymeric materials were extended to plant scale study to justfy the suitability. Both the samples, one anionic (caflo) and the other a mixture of catioinc, anionic and non-ionic (polymers) were supplied by the private houses viz. Product Development Council, Panihati and Jalan Enterprise. The results of the experiments are given below :

TABLE :—1.(A) FOR OPTICAL CLARIFICATION

Name of Polymer	Initial Turbidity of River Water in p.p.m.	Actual alum requirement in g.p.g	Requirement of alum along with the polymer in g.p.g	Dosage of polymer along with alum in p.p.m.
CAFLO	800	2.0	1.00	0.1
Polymix	1200	3.2	1.00	0.05

The exact constitution and nature of polymers were not supplied by the suppliers to maintain their trade secrecy. Both the products were not verified by 'Toxicity Test', hence those were not recommended for daily application, although the mechanism of polymeric action was well supported. The point of application was the clarifloccuIation plant drawing approximately 12 million gallon of river water per day. The superior clarifying capacity of the anions is due to their high molecular weight and degree of polymerization[7]. The anionic polymers help to shift (ζ-potential to the electronegative direction and such undesirable shift of) ζ-potential is counterbalanced, simultaneously by their capacity to attach several microfloc particles resulting in a mechanical and electrical interlocking[8].

Fig. 1(b) represents the characteristics of 3-type of polyelectrolytes as aids to either coagulation or flocculation. Both cationic and anionic aids beyond the optimum dosage for coagulation effect 'charge reversal' and sometimes undesirable shift of potential which cause deflocculation of floc particles. The non-ionic PEG, however, can not cause potential change after the addition of the same beyond optimum dosage and thus this curve becomes parallel[7,8] after the optimal dosage.

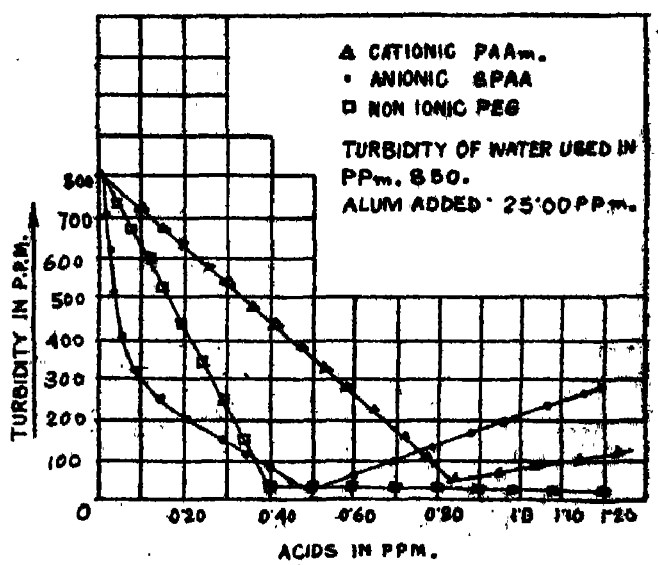


Fig. (1b)

The mechanism of coagulation and flocculation by polyelectrolytes[8] has been verified from the viscometric study of clay ~ SCMC interaction (Fig. 1c). Here non dialysed river clay ~ SCMC interaction in terms of η vs t is shown the steeper portion (minimum slope of the curve) represent the zone of SCMC clay interaction which obviates coagulation. This is also evident from the figure where subsequent rise in curve is shown just after the interaction. The interactions in three types of Clay-Al—Poly are identical *eg.* as Clay-Al-HA (Greenland[10]) [Al = Aluminium Ion, Poly = polyelectrolyte, HA = humic

TABLE—1 INFLUENCE OF DIFFERENT POLYELECTROLYTES IN PRESENCE/ABSENCE OF ASH/SLUDGE/CARBON IN REDUCTION OF ALUM DOSAGE AND BACTERIAL POPULATION (MPN)

Turbidity of Samples in p.p.m.	Alum (alone) in p.p.m.	Alum required for optimal coagulation with						
		0.5.p.p.m. SPAA only	0.5.p.p.m. SCMC only	0.5.p.p.m. PAAm only	0.5. p.p.m. PEG only	0.5 p.p.m. SPPA+ 500 p.p.m. ash	0.5 p.p.m. SCMC+ 500 p.p.m. ash	0.5 p.p.m. PAAm+ 500 p.p.m. ash
817	36.40	25.00	25.00	28.00	3.200	21.05	22.50	25.00
984	35.70	25.00	26.00	27.00	31.00	21.50	23.75	26.00
1000	37.80	26.00	29 00	32.00	33.25	25.85	27.35	29.00
1083	42.00	31.00	35.25	38.00	39.00	25.00	27.00	30.00
1108	50.80	32.25	38.25	40.00	46.60	26.50	28.00	32.28
1600	56.00	44.00	46.00	49.35	52.00	43.00	45.17	47.39
1700	58.00	46.83	49.00	51.35	55.90	44.50	46.07	49.00

Alum required for optimal coagulation with								
0.5 p.p.m. PEG+ 500 p.p.m. ash	0.5 p.p.m. SPAA+ 250 p.p.m. Sludge	0.5 p.p.m. SCMC+ 250 p.p.m. Sludge	0.5 p.p.m. PAAM+ 250 p.p.m. Sludge	0.5 p.p.m. PEG+ 250 p.p.m. Sludge	0.5 p.p.m. SPAA+ 100 p.p.m. carbon	0.5 p.p.m. SCMC+ 100 p.p.m. carbon	0.5 p.p.m. PAAm+ 100 p.p.m. carbon	0.5 p.p.m. PEG+ 100 p.p.m. carbon
28.10	25.50	26.95	28.00	30.25	19.25	21.00	22.50	25.35
29.00	27.00	29.00	30.15	32.00	19.00	21.00	23.00	27.00
30.28	28.50	30.25	32.45	35 00	20.50	22.00	24.80	28.47
32.00	30.19	31.13	33.56	36.21	20.00	23.25	25.61	29.25
33.61	30.32	31.05	34.13	37.50	20.25	24.90	27.00	30.13
50.12	45 00	46.12	48.25	50.16	37.05	39.21	40.98	42.13
52.11	47.37	47.85	50.49	51.16	41.25	43.17	45.23	46.80

Turbidity in p.p.m.	Alum (alone) in p.p.m.	Bacterial population (i.e. MPN) in different treatment x 10^{-8}/100 ml				Alum required in treatment				MPN in Alum (only) treated/100 ml
		Alum+ 0.5 p.p.m. SPAA+ 500 p.p.m. ash	Alum+ 0.5 p.p.m. SCMC+ 500 p.p.m. ash	Alum 0.5 p.p.m. PAAM+ 500 p.p.m. ash	Alum+ 0.5 p.p.m. PEG+ 500 p.p.m. ash	(a)	(b)	(c)	(d)	
(A) 1000	37.80	0.025	0.040	0.080	0.720	25.85	27.35	29.00	30.23	0.09
(B) 1200	40.50	0.012	0.020	0.050	0.430	26.00	28.00	33.50	35.00	0.06
(C) 1400	50.50	0.080	0.100	0.130	0.140	38.60	40.25	42.75	44.85	0.15

acids like humic, fulvic and hymatomelanic acid etc.] The higher flocculating capacity of non-ionic PEG. is probably due to ready hydration of hydrophilc molecular like other non-ionic[7]. n_{sp}/conc vs. n_{sp} curve is (Fig. 1c) slightly different from that of dialysed clay interaction and is due to presence of non clayey materials in the raw water.

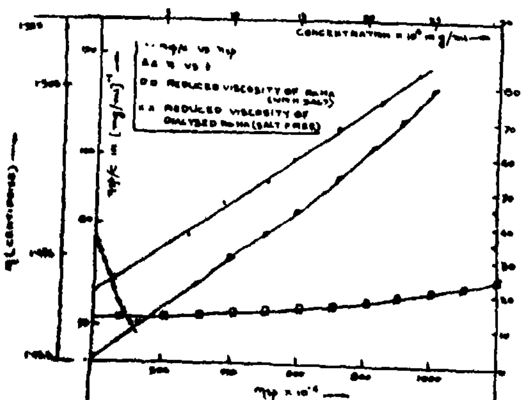


Fig. 1(c)

The studies with humic acids along with SPAA as a model system are shown in Table 2. From the comparison of nature of settling and floc formation capacity by the three sodium salts of humic acids fractions it appears that they may be placed in the order : SPAA> NaHyA> NaHA. The superior flocculating character of NaHyA to NaHA as also HyA to HA is attributed as due to the relative flexibility in structure and case of availability of functional groups[11] for complexation. Use of fly-ash in such system enhances the flocculation capacity through the formation of ash organic matter and ash-clay adsorption complex. Moreover, this helps to remove residual organic load that might ultimately invite bacterial proliferation. The polyelectrolytic behaviour of these humus salts was verified from the viscometric study n_{sp} /C vs. C in salt free and 0·1 N KCl media in Fig. 1c.

No direct attempt has yet been made to calculate the economy of the coagulation aided by polymeric materials. Indirectly it can be well ascertained in terms of alum reduction : Approximation from laboratory as well as plant scale study reveals that about 1/50th part (at the maximum) of alum dosage can well substitute 50% of actual alum requirement. Again the price of synthetic polymer on an average is 20 times greater than basic alum. Hence, the nett saving in this case will more than 50%. In case of humic substances, the cost price largely depends on the economic extraction from humified coal.

TABLE—2 INFLUENCE OF NaHyA, NaHA, NaPAA TOGETHER WITH ASH/ACTIVATED CARBON IN CLARIFICATION OF RIVER WATER IN TERMS OF ALUM REQUIRED/TIME OF CLARIFICATION

Turbidity of water samples in p.p.m.	Alum reqd. to make optimal **coagulation in p.p.m.	*"For Optimal coagulation : Alum reqd. with (in p.p.m.) 1.5 mg/lit. of NaHyA (a)	1.5 mg/lit. of NaHA (b)	1.5 mg/lit. of NaPAA (c)	1.5 mg/lit. of NaHyA (d)	1.5 mg/lit. of NaHA (e)	1.5 mg/lit. of NaPAA (f)	Time taken for clarification in (a)	(b)	(c)	(d)	(e)	(f)
		in presence ot 50 mg of ash			in presence of active carbon of 100 mg.								
817	36.40	25.00	30.25	21.05	24.76	26.00	19.25	8	10	3	6	9	3
984	35.70	23.50	27.85	21.50	22 25	24.00	19.00	9.5	12	3	8	10	3
1083	42.00	26.00	29.05	25.00	25.00	28.25	20.00	12	15	3	9	10	3
1108	50.80	27.00	31.25	25.50	25.00	29.75	20.25	10	12	3	10	12	3.5
1000	37.80	28.00	33.25	25.85	27.25	31.35	20.50	10	12.5	3.5	10	12	3.5
1600	56.00	45.00	46.50	43.00	43.50	46.00	37.05	10	15	4.5	10	12.5	—
1700	58.00	48.00	50.00	44.50	46.25	49.05	41.25	10	15	4.5	12	15	4.5

* Study was carried out throughout all the representative seasons of the year and an average of 25 samples was taken for each alum dosage fixation.

** Water used were of varied physicochemical characteristics influencing the alum dosage in different seasons

COMPARATIVE INFLUENCE OF NaHyA/NaHA AGAINST HyA/HA IN CLARIFICATION OF RIVER WATER TOGETHER WITH REMOVAL OF BACTERIA (COLIFORM ORGANISM) IN CASE OF SOME REPRESENTATIVE SAMPLES OF THE YEAR

Turbidity of water samples on p.p.m.	Alum required in p.p.m. (A)	*For Optimal Coagulation : alum reqd. with ash/carbon 1.50 mg/lit. of NaHyA (B)	1.50 mg/lit. of HyA (C)	1.5 mg/lit. of NaHA (D)	1.50 mg/lit. of HA (E)
1000	37.80	25.00	28.90	29.00	34.50
1200	45.50	30.00	35.65	33.00	41.25
1400	50.50	33.75	37.00	36.25	46.00

** Bacterial population in MPN from 100 ml. × 1000 (A)	(B)	(C)	(D)	(E)	in untreated water	Bacterial population in MPN per 100 ml. × 1000 (A)	(B) carbon treatment	(C)	(D)	(E)
0.09	0.12	0.20	0.12	0.25	9	0.05	0.08	0.12	0.09	0.18
0.06	0.08	0.10	0.10	0.12	6	0.06	0.09	0.08	0.07	0.08
0.15	0.30	0.50	0.40	0.50	15	0.11	0.20	0.32	0.28	0.24

* An average of 25 samples were taken in each dosage determination.

** Bacterial population in MPN were determined taking average of 20 samples.

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Heterocyclic Quinones. Part II : Synthesis of Benzo-(1 : 2-b, 4:5-b′)- dibenz (h,h′) Pyrrocoline Quinones

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A series of unsymmetrical disubstituted benzo-(1 : 2-b, 4 : 5-b′)-dibenz(h, h′) pyrrocoline quinones have been synthesised by condensing chloranil with active methylene compounds and quinoline which gave only the *trans* form of the compound as shown by colour reaction and TLC. The deep colour of these compounds is attributed to the betaine structure as one of the contributing form.

IN a previous communication[1] we have described the synthesis of benzo-(1:2-b, 4:5-b′)-dibenz(f,f′) pyrrocoline quinones. This reaction has been extended to the synthesis of benzo-(1:2-b, 4:5-b′)-dibenz (h,h′) pyrrocoline quinones by the reaction of chloranil with active methylene compounds and quinoline. The structure of these compounds has been established by affording evidence based on colour reactions with concentrated sulphuric acid[2], which have also been used to distinguish them from one another.

Interaction of chloranil with reactive methylene compounds and quinoline gave the respective 7:15-disubstituted benzo-(1:2-b, 4:5-b′)-dibenz(h,h′) pyrrocoline quinones (I). All these compounds did not melt upto 356° and gave blue to violet colour in concentrated sulphuric acid, which turned into red colour on basification followed by precipitation. The blue colour reappeared on addition of concentrated sulphuric acid. The colour reactions of these compounds indicate that the products should have *trans* configuration, which is the only product isolated in this case. The formation of *cis* structure in this case also, seems to be sterically hindered.

Experimental Procedure

All melting points have been determined on a Kofler instrument and are uncorrected. General procedure adopted for the preparation of the benzo-(1:2-b, 4:5-b′)-dibenz(h,h′)-pyrrocoline quinones is as given below.

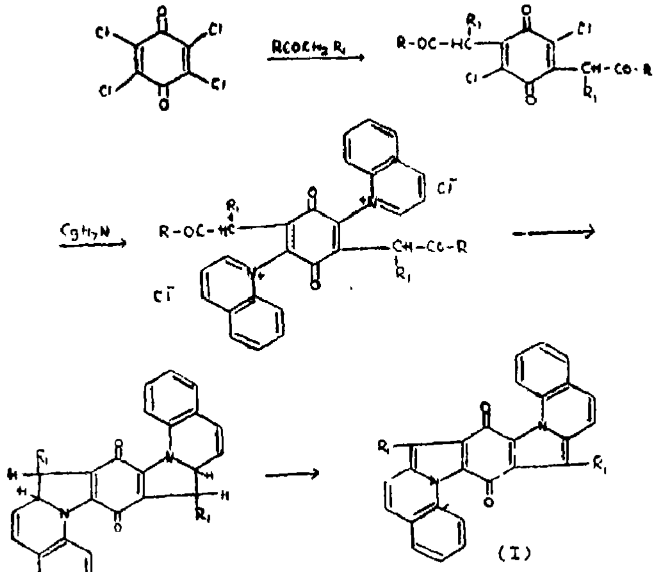
A mixture of chloranil (1 mole), reactive methylene compound (1 mole) and quinoline (1 mole) in 25-30 ml. absolute alcohol was heated under reflux on a water bath for 4 hours., when all the chloranil dissolved and a deeply coloured reaction mixture was obtained. The product separated on cooling was filtered and washed with ethanol, ether, hot water and then dried. The product was recrystallised from the desired solvent.

TABLE—1 7:15 DISUBSTITUTED-BENZO (1:2-b, 4:5-b′) DIBENZ(H,H′) PYRROCOLINE QUINONES(I)

S. No.	Active methylene compound used	Molecular formula	Crystallised form	Colour	M.P. °C	Found C%	Found H%	Found N%	Elemental analysis Required C%	Required H%	Required N%
1.	Ethyl acetoacetate	$C_{32}H_{22}N_2O_6$	Pyridine	Red	does not melt upto 356°	72.3	3.9	5.2	72.4	4.1	5.2
2.	Malonic ester	$C_{32}H_{22}N_2O_6$	Pyridine	Brown red	does not melt upto 356°	72.4	4.0	5.1	72.4	4.1	5.2
3.	Acetyl acetone	$C_{30}H_{18}N_2O_4$	Pyridine	Brown	does not melt upto 356°	76.5	3.8	5.9	76.5	3.8	5.9
4.	Benzoyl acetone	$C_{40}H_{22}N_2O_4$	Pyridine	Dark red	does not melt upto 356°	80.6	3.5	4.5	80.8	3.6	4.6
5.	Methyl cyanide	$C_{28}H_{14}N_4O_2$	Benzene +dioxane	Green	does not meltupto 356°	77.2	2.6	12.8	77.3	2.7	12.8

Mechanism :

The following reation machanism for the formation of 7:15 disubstituted-benzo(1:2-b, 4:5-b')-dibenz(h. h') pyrrocoline quinones has been given



whear

1. $R_1 = -COOCH_2 \cdot CH_3$
2. $R_1 - -COOCH_2C \cdot H_5$
3. $R_1 = -COCH_3$
4. $R_1 = -COC_6H_5$
5. $R_1 = -CN$

and it conforms the fact that it is the more electron attracting group R which is cleaved during the course of reaction as supported by experimental evidence.

The dyeing characteristics of these compounds is under investigation.

Acknowledgement

Thanks are due to Prof. R. C. Kapoor, Head of the Chemistry Department, for providing necessary laboratory facilities and to the U.G.C., New Delhi for the award of a Junior Research Fellowship to R.P.S.

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Studies on Oxazoles. Part I : Synthesis and Chlorination of Some new 2-Amino-4-substituted Oxazoles and their Use as Fungicides

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Some new 2-amino-4-substituted oxazoles synthesised by condensing various ketones with urea and using either bromine or iodnie as the condensing agent, have been subsequently chlorinated to yield the respective 5-chloro oxazole derivatives which have been assayed for their fungicidal activity against *Piricularia oryzae* (Cav.) the causative organism of rice plant, as the test fungus. A relation between fungitoxicity and chemical structure has been explored.

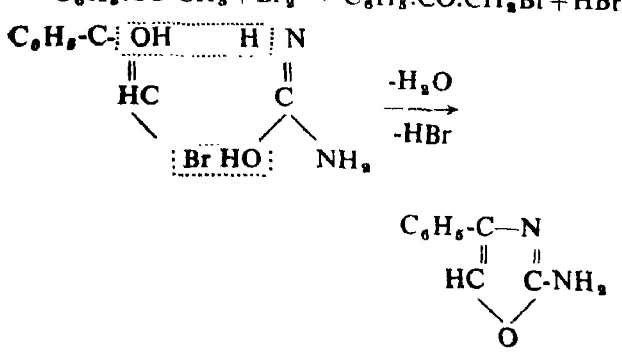
THE chemistry[1-3] and wide range of pharmaceutical properties of oxazole derivatives like hypertensive[4], analgesic, antiinflammatory[5,6], antibacterial, antiviral[7], antitubercular[8], anticonvulsant[9], urinary tract infections[10] and similar such diseases have been cited in the liteature.

The method of preparation of oxazole, first reported by Cornforth and Cornforth[11] has been subsequently modifed.[12,13] Since then many new methods of synthesising the substituted oxazoles have been developed[14]. One of the methods of synthesising the 2-amino-, and 2-*N*-substituted amino oxazoles is by the reaction of various alpha-haloketones with urea[15]. The relative inaccessibility of the alpha-haloketones is a major draw back of this method for its general use in preparing these oxazoles.

In view of this, an attempt has been made to find out the appropriate conditions under which 2-amino oxazoles can be synthesised using simple and readily available starting materials.

The present paper deals with the synthesis of some 2-amino-4-substituted oxazoles from urea and an appropriate ketone using either bromine or iodine as the condensing agent.

$$C_6H_5.CO.CH_3+Br_2 \rightarrow C_6H_5.CO.CH_2Br+HBr.$$



It has been observed that both bromine and iodine are able to bring about this reaction. But bromine is found to be more effective as regards the time of condensation as well as the yield of the end product.

It is well known that, chloro compounds belonging to the azole class are commercially used as fungicides[16]. In view of this fact the parent oxazoles prepared here have been chlorinated with dry chlorine gas in acetic acid medium after protecting the amino group by forming the corresponding hydrochloride salts. In each case, a monochloro derivative resulted.

In an identical type of reaction, in case of 2-amino-4-substituted thiazoles, the chlorine atom has been found to occupy C_5 position as the activity of this position is maximum, more so, when there is a polar substituent at C_2 position[17]. In that case, it has been shown that the polar effect of the substituents at C_2 and C_4 position[18] direct the incoming chlorine atom to C_5 position of the thiazole nucleus. This assumption gains further support from the fact that when 2-amino-4-aryl thiazoles are brominated, 5-bromo thiazoles are resulted in each case. The bromine dose not occupy any other position except C_5 of the thiazole moiety[19] even though there are activating oxygenated group in the phenyl nucleus attached to C_4 position.

In analogy with the above established experimental observations, in the case of the oxazoles, the chlorine atom is assumed to have occupied the C_5 position which is free and is most active. In case of the 2-amino oxazoles, the orienting effect of the $-NH_2$ group enhances the activity of C_5 position ; this being the para-position with respect to the $-NH_2$ group.

That the activity of the C_5 position is maximum has also been established from the following facts. The reaction of oxazoles with electrophiles shows that the order of reactivity is $C_5 > C_4 > C_2$ and bromination of oxazole ring is in conformity with this[10]. A consideration of the charge densities at these positions shows position 5 to be slightly more reactive than position 4 and electrophillic attack at these positions is facilitated when the ring is activated by electron donating substituent like $-NH_2$ group. Hence in the chlorination of the 2-amino-4-substituted oxazoles, the chlorine atom has assumed to have occupied position 5 as the position 4 is already blocked and the activity of posstion 5 has been enhanced due to the $-NH_2$ group at position 2.

That the chlorine atom goes to position 5 is further supported on the following experimental observations. When 2-amino-4-phenyl oxazole is treated with diazotised aniline, coupling reaction takes place giving rise to an orange coloured azo dye in which the phenyl azo group is linked to the C_5 position of the oxazole moiety. But 2-amino-4-phenyl-5-chloro oxazole resulted from the chlorination of the above oxazole fails to undergo coupling reaction at all which indicates that in the later case C_5 is not free and is blocked by the chlorine atom. When the chloro oxazole is refluxed for ten hours with HCl (1:3) and allyl alcohol the original chlorine free oxazole is obtained which responds to the diazo coupling reaction.

Experimental

1. *2-Amino-4-phenyl oxazole* :

In a clean and dry conical flask, acetophenone (6 g) was taken. To it bromine (8 g) in dry benzene (40 cc) was added very slowly in small proportion while keeping the flask in sun light. The mixtures was vigorously shaken till the colour due to bromine was discharged. To this solution, urea (15 g) was added. The flask was fitted with a double surface reflux condenser and the mixture was refluxed in a water bath for 27 hrs. The condenser was the removed and the mixture was further heated for a period of 3 hrs. The reaction product was then cooled, repeatedly extracted with ether to remove the unreacted ketone and bromine to save it from becoming gummy. The product was then basified with conc. ammonia and kept over night. It was then filtered and the product was repeatedly washed with water, dried and finally recrystallised from water : alcohol (1:1 v/v).

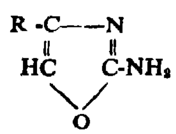
Comparative study with Br_2 and I_2 as condensing agent in different solvents.

Reactants	Solvents	Period of heating in hours	Colour	Yield %
Urea + Aceto-phenone + bromine	Benzene	24	Light yellow	55
-do-	-do-	30	-do-	60
-do-	D.M.F.	30	-do-	60
Urea + Aceot-phenone + iodnie	-do-	30	-do-	20
-do-	Benzene	30	-do-	20

The compounds showed the same m.p., m.m.p. and super imposable IR curve with a peak at 1555 cm^{-1}, characteristic of the $-N=C-O-$ ring stretching frequency. The homogenity and purity of the compounds were tested through tlc. The compounds were developed on a thin layer of silica gel-H having a slurry thickness of 250μ by the ascending technique and after development the compounds were detected as fluorescent spots under U.V. light. The R_f values of the compounds were found to be same (R_f 0.81 in benzene-methanol, 50 : 50 v/v ; and 0.89 in benzene-isoamyl alcohol, 50 : 50 v/v).

The colour, yield, m.p. and analytical data of such 2-amino-4-substituted oxazoles are given in Table-1(Sl no.1 to 10).

TABLE—1



Sl. No.	Nature of R	Colour	Yield (%)	M.P. °C	Cl. (%) Found	Cl. (%) Calcd.	N (%) Found	N (%) Calcd.	Fungicidal result Parts in ppm for 50% germination.
1.	C_6H_5-	L.Y.	60	140	-	-	16.85	17.50	15
2.	*p*-$Cl.C_6H_4$-	L.Y.	50	190	17.85	18.25	13.80	14.39	5
3.	*p*-Hydroxy C_6H_4-	G.Y.	50	205	-	-	15.45	15.90	15
4.	*o*-OH C_6H_4-	B	50	167	-	-	15.38	15.90	15
5.	*p*-$OCH_3C_6H_4$-	Y.B.	45	180	-	-	14.62	14.73	14
6.	α-$C_{10}H_7$-	B	60	112	-	-	13.61	13.33	7.5
7.	β-$C_{10}H_7$-	Y.B.	80	162	-	-	13.73	13.33	6
8.	*p*-$NO_2C_6H_4$-	B	56	190	-	-	-	-	15
9.	*p*-$CH_3C_6H_4$-	Y	65	160	-	-	15.57	16.09	24.5
10.	C_4H_3S-	B	70	90*	-	-	16.62	16.86	12.5

L=Light, Y=Yellow, G=Green, B=Brown

* Denotes decomposition.

2. *2-Amino-4-phenyl-5-Cl-oxazole* :

2-Amino-4-phenyl oxazole(2 g) was treated with conc. HCl (3ml) and the hydrochloride salt formed was dissolved in glacial acetic acid (25 ml). To this solution, dry chlorine gas was passed in a slow and steady rate. The deep colour of the solution gradually faded. The chlorination was continued till solid separated out. The reaction mixture was poured into water and the precipitate was then basified and kept over-night. The chloro oxazole formed was then filtered, washed with water till it was free from chlorine, then dried and recrystallised from alcohol : water (1 : 1 v/v). The colour, yield, m.p. and analytical data of the chloro oxazoles are given in Table-2.

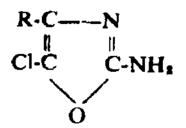
(b) The presence of chlorine augments fungicidal activity and this increases with increase in the no. of chlorine atoms in the molecule.

(c) The presence of α-naphthyl and β-naphthyl groups at position 4 increases fungicidal activity.

(d) The presence of $-CH_3$ and $-NO_2$ groups does not help towards fungitoxicity. The deactivating effect of $-NO_2$ group is well compensated by introduction of chlorine atom.

(e) When substituent like -OH group is present in the aryl nucleus at C_4 position in the chloro derivatives the compounds are very much active.

TABLE—2



Sl. No.	Nature of R	Colour	Yield (%)	M.P. °C	Cl. (%) Found	Cl. (%) Calcd.	N (%) Found	N (%) Calcd.	Fungicidal result Parts in ppm for 50% germination.
1.	C_6H_5-	L.Y.	83	205	17.91	18.25	13.92	14.39	3.0
2.	p-Cl.C_6H_4-	Y.	80	155	30.85	31.00	11.85	12.22	1.5
3.	p-OH.C_6H_4-	Y.B.	65	183	16.71	16.86	12.93	13.30	1.0
4.	o-OH.C_6H_4-	B.	60	126	16.69	16.86	12.89	13.30	5.0
5.	p-OCH_3.C_6H_4-	G.W.	82	225	15.68	15.81	12.11	12.47	8.3
6.	α-$C_{10}H_7$-	C.B.	85	105	14.38	14.51	11.01	11.45	4.3
7.	β-$C_{10}H_7$-	Gr.	85	149	14.31	14.51	11.10	11.45	4.3
8.	p-NO_2.C_6H_4-	B	72	175	14.71	14.82	17.21	17.53	4.2
9.	p-CH_3.C_6H_4-	L.Y.	85	164	16.98	17.02	13.21	13.42	16.0
10.	C_4H_3S-	B	80	>250	17.50	17.70	13.73	13.96	8.3

L = Light, Y = Yellow, G = Green, B = Brown, W = White, C = Chocolate, Gr = Grey.

Fungicidal Test :

The synthesised oxazoles and the chloro oxazoles have been assayed for their fungicidal activities against *Pricularia oryzae* (Cav.), the causative organism of rice blast, as the test fungus. The method of Montgomery and Moore[21] with slight modification was used for the fungicidal assay of these compounds. The spores were kept in contact with the chemicals at different dilutions for 24 hrs and the percentage of germination was studied in that duration. The dilution in p.p.m. of the compounds for 50 per cent germination of the fungus has been given in Table-1. The analysis of the fungicidal results showed a definite in pattern existing between fungitoxicity and the chemical structure in general. The following generalisations in this respect may be derived.

(a) Both the oxazole and the chloro oxazoles have got considerable fungicidal activity, in general against *Piricularia oryzae*(Cav.) while compounds of Sl.no.2, 6, 7, of Table 1 and 1, 2, 3, 4, 6, 7 and 8 of Table 2 are very active.

(f) Heterocyclic group like thienyl at C_4 position does not seem to enhance fungicidal activity.

(g) The order of activity of the substituents at position 4 in the oxazoles is $-Cl.C_6H_4 > -C_{10}H_7 \sim -C_4H_3S > -OCH_3.C_6H_4, -NO_2C_6H_4, -C_6H_5, -OH{\cdot}C_6H_4 > -CH_3.C_6H_4$.

Acknowledgement

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Heterocyclic System II[1]. Electrophilic Substitution on 1-Phenyl-4-(2-hydroxybenzoyl)pyrazole

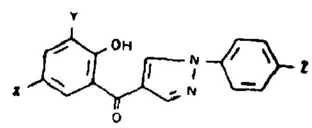
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A comparative study as to the ease of substitution in phenol, pyrazole and benzene has been done by subjecting 1-phenyl-4-(2-hydroxybenzoyl)pyrozole (I) to halogenation and nitration. Halogenation (mono-or di-) takes place at the phenol moiety. Chlorination and bromination in acetic acid medium furnish 1-phenyl-4-(3,5-dihalogeno-2-hydroxybenzoyl)pyrazole(III) and (VI) respectively. Bromination and iodination in refluxing benzene medium produce the respective 1-phenyl-4-(5-halogeno-2-hydroxybenzoyl)pyrazole (IV) and (V). The pyrazole (I) produces 1-(*p*-nitrophenyl)-4-(2-hydroxybenzoyl)pyrazole (IX) on nitration with mixed acid.

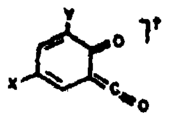
PYRAZOLE nucleus is highly stabilised and possesses many properties of aromatic compounds. It has been compared to some extent with benzene with regards to ease of substitution. That pyrazole is more easily substituted than benzene is seen in the bromination of 3-phenyl-5-chloropyrazole to 3-phenyl-4-bromo-5-chloropyrazole[2]. Even 1-phenylpyrazoles that contain a benzene nucleus seemingly as activated as N-acylated aniline also undergo halogenation at position 4 of the pyrazole ring. Though substitution at 4 position of pyrazole is very common, that at the other position when position 4 is blocked is not rare. Bromination of 1-phenyl-3-methyl-4-bromopyrazole gave a 4,5-dibromocompound[4]. This report goes against the finding of Finar *et al*[5] who obtained 1-(*o*-bromophenyl)-3-methyl-4-bromopyrazole, not the 4, 5-dibromocompound, by bromination of 1-phenyl-3-methylpyrazole. There are many other contradictory reports and/or uncertanties about the position of substitution in 1-phenylpyrazole system,[6,7], and there is not a single datum in literature to show how 1-phenylpyrazole system, the pyrazole ring of which is deactivated by the presence of an electron withdrawing group, will behave towards substitution by halogens. Again, though it is generally believed that pyrazole is less susceptible than phenol towards electrophilic substitution[8], no detailed study about the ease of their substitution has been done. So we wanted to throw some new lights on the points raised above and to make simultanously a comparative study about the relative ease of substitution in an activated benzene, a pyrazole deactivated by the psesence of an electron withdrawing group at position 4 and a deactivated phenol, all the moieties remaining incorporated in the same substrate. Such a substrate is offered by 1-phenyl-4-(2-hydroxybenzoyl)pyrazole(I).



	X	Y	Z
I	H	H	H
II	Cl	H	H
III	Cl	Cl	H
IV	Br	H	H
V	I	H	H
VI	Br	Br	H
VII	Cl	Br	H
VIII	NO_2	H	H
IX	H	H	NO_2

The pyrazole (I) was subjected to chlorination, bromination and iodination, and the mass spectral analysis of the halogenated products was done. In addition to the molecular ion (base peak), four other principal fragments A], [B], [C] and [D] were obtained[1]. These fragments clearly indicated that substitution (mono- or di-) had taken place at the phenol moiety of the pyrazole (I).

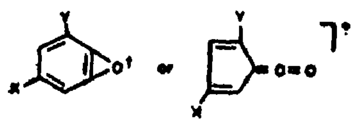
Chlorination of the pyrazole (I) in warm acetic acid gave a dichlorocompound. That one of the two chlorine atoms in this dichlorocompound was located in *p*-position of the hydroxygroup, was proved by chlorinating 1-phenyl-4-(5-chloro-2-hydroxybenzoyl) pyrazole(II) when the same dichlorocompound resultedin. On general ground (mesomeric-effects of electron donating hydroxygroup and electron withdrawining carbonyl function), the structure



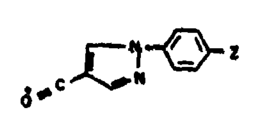
(A)



(B)



(C)



(D)

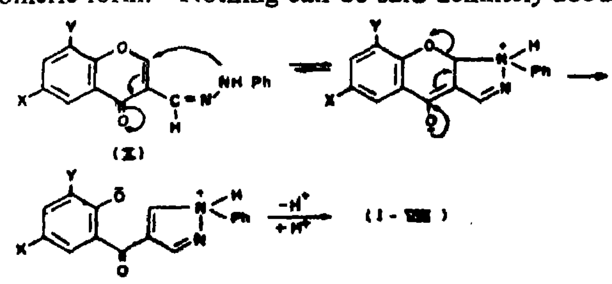
of 1-phenyl-4-(3,5-dichloro-2-hydroxybenzyol)pyrazole(III) was assigned to this dichlorompound. Its nmr spectrum τ —2.03(1H, br, ArOH), 1.53(1H, s, pyrazole H_5), 1.83 (1H, s, pyrazole H_3), 2.27 (1H, d, J 2Hz, ArH *ortho* to chloro- and carbonyl functions), 2.42 (1H, d, J 2Hz, ArH *ortho* to two chloro-groups) and 2.81 (5H, s, ArH), is also compatible with this structure (III). Bromination and iodination of the pyrazole(I) in refluxing benzene solution gave monohalogenated products, whereas bromination in acetic acid medium produced a dibromocompound. The structures (IV), (V) and (VI) were assigned to the monobromo-, monoiodo- and dibromo- products respectively. The structures (IV) and (VI) were also confirmed by independent syntheses. The structure of the iodo-product was deduced as (V) from analogy with the monobromocompound (IV). The chlorocompound(II) and the monobromocompound(IV) could be further brominated to the dihalogenated products(VII) and (VI) respectively. The pyrazole(I) could not be iodinated in acetic acid medium.

A cursory look at the structure of the substrate (I) would reveal that the carbonyl group deactivates both phenol and pyrazole almost to the same extent. So the substitution reaction of the compound(I) is tantamount to the comparison of the relative ease of substitution in at least 2-substituted phenol and 4-substituted pyrazole, if not proper phenol and pyrazole themselves, under absolutely identical conditions. The substrate(I) offers another advantage as to examine whether the activity of a slightly deactivated pyrazole is equal to, or more or less than that of N-acylated aniline. Halogenation, particularly dichlorination and dibromination data, clearly show that phenol is much more reactive than pyrazole as well as the benzene nucleus of 1-phenylpyrazole.

Nitration of the pyrazole (I) with mixed acid gave a mononitro derivative. Had the nitration the same trend as that of halogenation, one would expect the formation of 1-phenyl-4-(2-hydroxy-5-nitrobenzoyl)pyrazole (VIII). An authentic sample of the pyrazole (VIII) was prepared, but it was found to be different from the nitration product of the pyrazole (I). Oxidative degradation of this nitroproduct to 1-(*p*-nitrophenyl)pyrazole-4-carboxylic acid[9] suggested it to have the structure of 1-(*p*-nitrophenyl)-4-(2-hydroxybenzoyl)pyrazole (IX), and the prepared authentic sample of 1-(*p*-nitrophenyl) pyrazole (IX) was found to be identical with it. The nitrosubstitution at the benzene nucleus of 1-phenylpyrazole (I) in preference to either at hydroxyphenyl or at pyrazole ring can be rationalised as follows. In concentrated sulphuric acid medium as used for nitration purpose, the phenol moiety undergoes at first sulphonation at *para* position to the hydroxy group (as in preparation of *o*-bromophenol from phenol[10]) and thus becomes deactivated, the sulphonic acid group being knocked off at a later stage during work up. Pyrazole ring of 1-phenylpyrazole is also deactivated[11] in acid medium by getting protonated at position[2], but the 1-phenyl moiety is little affected. It is also recorded in literature[12] that 1-phenylpyrazoles having electron withdrawing substituent as carboxylic attached to the pyrazole ring nitrate only in the *para*-position of the benzene ring. It may be further mentioned here that salicylic acid on nitration with 15% nitric acid yields 5-nitrosalicylic acid[13] whereas nitration of a solution of salicylic aicd in conc. sulfuric acid with mixed acid gave exclusively 3-nitrosalicylic acid[14] in our hand. This experiment clearly indicates that though salicylic acid is not completely deactivated in sulfuric acid medium, at least its position 5 is blocked by sulfonation. In nitration of the pyrazole (I) we obtained the nitro-product (IX) in 50% yield ; it might be the case that some 1-(*p*-nitrophenyl)-4-(2-hydroxy-3-nitrobenzoyl)pyrazole was also formed, which we failed to isolate.

1-Phenyl-4-(2-hydroxybenzoyl)pyrazole (I) and the authentic samples of the substituted pyrazoles(II, IV, VI and VIII) could be prepared by refluxing the phenylhydrazones (X) of properly substituted 4-oxo-4*H*-[1]benzopyran-3-carboxaldehydes in ethanolic potassium hydroxide solution[1]. Later on, it was found that generation of the aldehyde function by cleavage of the pyrone ring at C-2 with hydroxide anion[15] was not necessary for the formation of the pyrazole ring. The phenylhydrazones (X) on refluxing in glacial acetic acid gave rise to the desired pyrazoles. In this case, the intramolecular nucleophilic attack takes place at C_2 with concomitant opening of the pyrone ring as shown in Scheme 1.

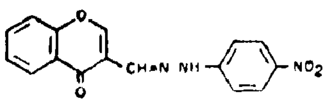
The cyclisation reaction as depicted in Scheme 1 demands that the hydrazones (X) must exist in Z-isomeric form. Nothing can be said definitely about



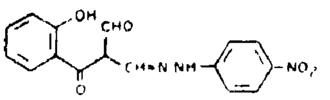
Scheme - 1

the stereochemistry of the hydrazones. Had they existed in E-form, they must have isomerised to Z-form under reaction conditions.

The preparation of 1-(*p*-nitrophenyl) pyrazole (IX) deserves special mention. *p*-Nitrophenylhydroazone (XI) of 4-oxo-4*H*-[1]-benzapyran-3-carboxaldehyde failed to produce the compound (IX) when refluxed in ethanolic potassium hydroxide solution. Here the intermediate aldehyde (XII)[15] perhaps underwent deformylation before the aldehyde function could combine with the phenylhydrazino group of weak nucleophilicity. The hydrozone (XI) evaded the conversion as depicted in Scheme I when refluxed in acetic acid, whereas the same conversion to the pyrazole (IX) was made possible by refluxing it in ethylene glycol. So it is certain that thermal energy rather than solubility of the hydrazones (X) and (XI) influences the cyclisation reaction.



(XI)



(XII)

Experimental

N.m.r spectra were measured with a Varian T60 60MHz spectrometer in $CDCl_3$ solution with TMS as internal standard. Mass spectra were determined with a Hitachi RMU-6L spectrometer at 80eV using the direct inlet system. Melting points were taken in open capilaries in a sulfuric acid bath. Pet. ether refers to the fraction of b.p. 40-60°.

Preparation of the pyrazoles (I, II, IV and VIII) : The phenylhydrazone (X, X=Y=H)[1] (0.50 g) was refluxed in glacial acetic acid for 1 hr., cooled and diluted with water. The precipitated solid was filterred and crystallised from ethanol in light yellow crystals (0.44 g) of *1-phenyl-4-(2-hydroxybenzoyl) pyrazole(I)*, mp. 113°, (lit.[1]. m.p. 113°)

Similar treatment of the phenylhydrazones (X)[1] of the properly substituted 3-formylchromones gave in approximately 80% yields the *pyrazole*(II), m.p. 146° (EtOH) (lit.[1], m.p. 145°), the *bromopyrazole* (IV), m.p. 154° ($CHCl_3$), and the *nitropyrazole* (VIII), m.p. 207° (EtOH).

Chlorination of the pyrazole (I) : Chlorine was passed into a warm solution of the pyrazole (I) (0.50 g) in acetic acid (10 ml) for 1 min. The solution was cooled in ice when *1-phenyl-4-(3,5-dichloro-2-hydroxybenzoyl)pyrazole* (III) separated as a solid (0.49 g). Crystallisation from chloroform gave lightly yellow crystals, m.p. 182-4° ; *acetate*, m.p. 121-2° ($CHCl_3$).

The *pyrazole* (II) (0.60 g) was similarly chlorinated to the *dichlorocompound* (III) (0.60 g).

Bromination of the pyrazole(I) in benzene medium : The pyrazole (I) (0.10 g) wag refluxed with bromine (0.5 ml) in benzene (20 ml) for 3 hr. The mixture was then cooled, washed with sodium bisulfite solution and water. Benzene layer was dried (Na_2SO_4) and concentrated to afford *1-phenyl-4-(5-bromo-2-hydroxybenzoyl) pyrazole* (IV) (0 09 g), m.p. and m.m.p. 154° ($CHCl_3$) ; *acetate*, m.p. and m.m.p. 132° ($CHCl_3$-Pet. ether).

Iodination of the pyrazole (I) : The pyrazole (I) (0.40 g) was refluxed with iodine (1.0 g) in benzene (40 ml) for 4 hr. Similar processing of the reaction mixture as in case of bromination yielded yellow crystals of *1-phenyl-4-(5-iodo-2-hydroxybenzoyl)pyrazole* (V) (0.39 g), m.p. 143° (EtOAc), ν_{max} (nujol) 1670 (w,-CO) ; *m/e* 390 (M^+), 246, 218, 171 and 144. Its acetate was a low melting solid.

Bromination of the pyrazole (I) in acetic acid medium : The pyrazole (I) (0.40 g) was refluxed with bromine (3 ml) in acetic acid (10 ml) for 3 hr., then poured into water (40 ml). *1-Phenyl-4-(3, 5-dibromo-2-hydroxybenzoyl) pyrazole*(VI) (0.44 g) was collected by filtration. Recrystallisation from chloroform afforded needle shaped yellow crystals, m.p. and m.m.p. 179° ; τ-2.41(1H, br, ArOH),1.58 (1H, s, pyrazole H_3), 1.90 (1H, s, pyrazole H_5), 2.08 (1H, d, J 3 Hz, ArH *ortho* to bromo and carbonyl groups), 2.37 (1H, d, J 3 Hz, ArH *ortho* to two bromo groups) and 2.77 (5H, s, ArH) ; *m/e* 422, 420, 418, 280, 278, 276, 171 and 144 ; *acetate*, m.p. and m.m.p. 165-8° ($CHCl_3$).

The *bromopyrazole*(III) (0.12 g) and the *chloropyrazole* (II) (0.10 g) on similar treatment with bromine afforded respectively the *dibromocompound* (VI) (0.11 g) and the *chlorobromocompound* (VII) (0.09 g), m.p. 171° ($CHCl_3$) ; *acetate*, m.p. 147° ($CHCl_3$).

Nitration of the pyrazole (I) : The pyrazole (I) (0.20 g) was added in small lots to a well cooled mixture of conc. sulfuric acid (5 ml) and conc. nitric acid (5 ml). After the addition was over, the mixture was warmed on a water bath for 30 min., cooled and then poured over ice. The separated solid was filtered and crystallised from ethanol to afford yellow crystals of *1-(p-nitrophenyl)-4-(2 hydroxybenzoyl)pyrazole* (IX) (0.12 g), m p. and m.m.p. 191-3° ; *acetate*, m.p. and m.m.p. 150° ($CHCl_3$).

Oxidation of the nitrocompound (IX) : The above nitrophenylpyrazole (IX) (0.50 g) was oxidised with chromic acid according to the procedure[1] described for the oxidation of the parent pyrazole(I) to furnish

1-p-nitrophenylpyrazole-4-carboxylic acid (0.12. g), m.p. 247° ($CHCl_3$) (lit.[9], m. p. 250°). Its mass spectrum showed peaks at *m/e* 233 (M^+), 216 (M-OH), 203 (M-NO) and 187 (M-NO-OH).

Authentic sample of 1-phenyl-4-(3,5-dibromo-2-hydroxybenzoyl)pyrazole (VI) ;

2,4-Dibromophenol was prepared according to the method of Pope *et. al.*[16]. On adding bromine (120 g, 39 ml) dissolved in hydrobromic acid (40 ml) to a suspension of phenol (35.5 g) in hydrobromic acid (10 ml) at below 0° was obtained 2,4-*dibromophenol* (47 g). m.p. 40° (lit.[16], m.p. 40°) which on being refluxed with acetic anhydride (30 ml) and a few drops of conc. sulphuric acid afforded 2,4-*dibromophenyl acetate* (49.0 g) b. p. 160-5°/15 mm. The above acetate (30 g) was subjected to Fries rearrangement[17] and after usual work up 3,5-*dibromo-2-hydroxyacetophenone* (14.0 g), m.p. 106° (lit.[17], m.p. 110°) was obtained.

A solution of the above acetophenone (14.0 g) in DMF (10.0 ml) was added to the formylating complex prepared from phosphorus oxychloride (8.20 ml) and DMF (20.0 ml)[18]. After usual workup, *6,8-dibromochromone-3-aldehyde* (6.0 g), m.p. 174° (lit.[18], m.p. 177-8°) was obtained.

A mixture of the above chromone-aldehyde (3.30 g, 0.01 mole) and phenylhydrazine (1.08 g, 0.01 mole) in ethanol (20.0 ml) was warmed when the *hydrazone* (X, X=Y=Br) (4.20 g) separated out, which without further purification was refluxed in acetic acid (15.0 ml) for 2 hr to afford the *pyrazole* (VI) (3 98 g), m.p. 179° ($CHCl_3$) ; *acetate*, m.p. 168° ($CHCl_3$).

Authentic sample of 1-(p-nitrophenyl)-4-(2-hydroxybenzol)pyrazole (IX) : A mixture of 3-formylchromone (1.74 *g*, 0.01 mole) and *p*-nitrophenylhydrazine (1.53 g, 0.01 mole) was refluxed in ethanol for 1 hr. On removel of ethanol was obtained the *hydrazone* (XI) (3.0 g), m. p. 248-50° (acetic acid), which was refluxed with ethylene glycol (15.0 ml) for 6 hr., cooled and diluted with water. The precipitated solid was filtered and crystallised from ethanol to afford the *nitrophenylpyrazole* (IX) (2.6 g), m. p. 191° ; *acetate*, m. p. 150° ($CHCl_3$)

3-Nitrosalicylic acid : To a cooled solution of salicylic acid (1.0 g) in conc. sulfuric acid (20 ml) was added conc. nitric acid (10 ml) slowly. After the addition was over, the mixture was warmed for 14 min, then poured over ice when *3-nitrosalicylic acid* (0.98 g), m.p. 126° (water) (lit[14]., m.p. 125°), *amide*, m.p. 142° (lit[14]., m.p. 145°) was obtained.

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Possible Antifertility Compounds-Part II : Synthesis of 1, 2, Disubstituted Benzimidazoles

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Synthesis of new benzimidazole derivatives, derived from the condensation of o-phenylenediamine and N-substituted amino acids have been reported. Some of these compounds have been subjected to Mannich-type condensation to yield 1-salicylamido-methyl-2-phthalimido-alkylbenzimidazoles. Two compounds were tested for antiestrogenic activity and one was evaluated as a male antifertility agent but they were found to be ineffective.

SUBSTITUTED benzimidazoles have been investigated as metabolic inhibitors in chicken sperm[1], in bacteria[2], in poliovirus[3], and in chicken embryos[4,5]. It has been postulated that substituted benzimidazoles could interfere with the production of nucleotides because of their similarity to vitamin[6] B-12 Later, 2-ethyl-5-methyl benzimidazoles were shown to inhibit Ribonucleic acid (RNA) synthesis in chicken embryo[6].

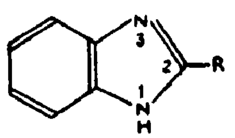


Fig. 1

It has been observed that benzimidazole itself (I, R=H) has very low activity[7]. Substitution at position 2 of imidazole enhances the activity. The simple alkyl, alkenyl and aryl substituents in the position 1 increase the antiviral activity. But modifications to the fused benzene ring destroy activity[7,8].

Spermatogenesis was arrested by substituted benzimidazoles[9] and by imidazoles substituted at position 1 by aryl group[10]. 2, 5-Dialkyl benzimidazole has been reported to reduce sperm motility[11]. 1, 2-Disubstituted benzimidazoles also cause nervous system (CNS) depression in experimental animals. Substitution of a methyl group instead of phenyl in position 2 led to the lowering of CNS depressant activity[8], and hetro analogs gave enhanced activity over simple aryl (e.g. phenyl, naphthyl) derivatives[12]. In addition, benzimidazoles could be explored for abortifacient, because of their teratogenic effect on chicken embryo[5].

The above studies prompted us to synthesize a number of previously unreported compounds, containing benzimidazole nucleus for antifertility testing. The position 2 was substituted with phenyl carboxamido alkyl and phthalimido alkyl groups. The phthalimido derivatives have been shown to inhibit fertility in male rats[13]. In few compounds, salicylamido methyl group substitution at position 1 was based on the previous observation that 1-hydroxy-2-phenyl benzimidazoles have the CNS depressant activity[8] and imidazole substituted at position 1 by aryl groups has antifertility activity in male rats[10].

Experimental

Phthaloyl/3:5-dinitro benzoyl-amino acids were obtained following the method of Vogel[14].

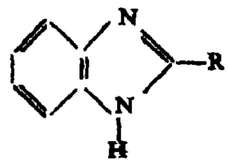
2-Phthalimido/3:5-dinitro benzamida-alkylbenzimidazoles :

A mixture of equimolar quantities of *o*-phenylenediamine and *N*-substituted amino acid was heated in an oil bath at 100-105° under reflux for 3-4 hours. It was cooled and treated with sodium bicarbonate solution (5%) to remove any unreacted acid. A pasty mass was obtained which was titurated with petroleum ether (60-80%) and the crude product thus obtained was recrystallized from appropriate solvent.

Various compounds thus synthesised are listed in Table 1.

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TABLE—1 2-SUBSTITUTED BENZIMIDAZOLE



Sl. No.	R	M.P. °C	Molecular Formula	% Analysis (Nitrogen) Calculated	Found
1.	2-[α(3′ : 5′-dinitrophenylcarboxamido)-ethyl]-	94°	$C_{16}H_{13}N_5O_5$	19.7	19.1
2.	2(3′ : 5′-Dinitrophenylcarboxamidomethyl)-	160°	$C_{15}H_{11}N_5O_5$	20.5	19.8
3.	2-*o*(3′ : 5′-Dinitrophenylcarboxamido-phenyl)-	250°	$C_{20}H_{13}N_5O_5$	17.9	18.4
4.	2-*p*(3′ : 5′-Dinitrophenylcarboxamido-phenyl)-	190°	$C_{20}H_{13}N_5O_5$	17.9	17.7
5.	2-Methyl phthalimido-	245°	$C_{16}H_{11}N_3O_2$	15.16	14.8
6.	2-[α-(phthalimido)-ethyl]-	220°	$C_{17}H_{13}N_3O_2$	14.38	15.2
7.	2-(1′-phthalimido-1′-isopentyl)-	228°	$C_{20}H_{19}N_3O_2$	12.61	12.1
8.	2-(1′-phthalimido-1′-isopentyl)-	250°	$C_{20}H_{19}N_3O_2$	12.61	13.2
9.	2-(1′-methyl histidynyl-1′-phthalimido)-	225°	$C_{20}H_{15}N_5O_2$	19.6	18.9
10.	2-[(1′-phthalimido-3′-benzimidazolyl)-propyl]-	105°	$C_{25}H_{19}N_5O_2$	16.6	16.4

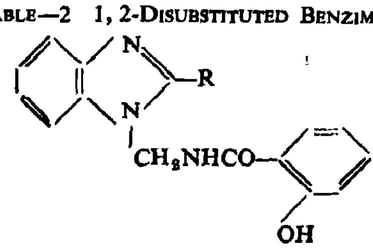
1-Salicylamido-methyl 1-2-phthalimido alkyl-benzimidazoles

2-Phthalimido alkyl-benzimidazole (0.006 *M*) was dissolved in the minimum quantity of ethanol by warming on a water bath. To this solutions, was added a mixture of formalin (0.012 *M*) and salicylamide in 10 ml of ethanol and a few drops of concentrated hydrochloric acid with constant stirring. After the addition was complete, the reaction mixture was further stirred for half an hour at room temperature and subsequently refluxed on a water bath for 4-5 hours. Ethanol was distilled off, and the crude product obtained was washed thoroughly with water. It was dried and recrystallized from suitable solvent.

Table-2 lists the various 1,2-disubstituted benzimidazoles.

female rats. The rats were overiectomized under pentobarbitone (30 mg/Kg I.P.) anaesthesia and rested for one week. On the eighth day the rats were divided in three groups. The first group was treated with 10 μg/Kg/day of Oestradioldipropionate intraperitonially for three days. Second and third groups were treated with 2-*p*-(3′:5′-dinitrophenyl carboxamido phenyl) benzamidazole (A) and 2-(3′ : 5′-dinitrophenyl carboxamido methl) benzamidazole (B) respectively. These compounds were suspended in gum acacia and were given at the doses of 100 mg/Kg orally along with 1 μg/100 gm of Oestradioldipropionate for three days. Afterwards all the animals were sacrificed and the uterus was removed from each animal and dried at 60° (Table 3). From these studies it appears that the test compounds have no significant effect on the uteri dry weight. The administration of potential antioestrogenic compounds results in drastic reduction in dry weight, RNA and protein synthesis.

TABLE—2 1, 2-DISUBSTITUTED BENZIMIDAZOLE



Sl No.	R	M.P. °C	Molecular Formula	% Analysis (Nitrogen) Calculated	Found
1.	(2-methyl-phthalimido)	92°	$C_{24}H_{18}N_4O_4$	13.2	13.7
2.	2(α-phthalimido ethyl)	140°	$C_{25}H_{20}N_4O_4$	12.7	11.9
3.	2-(1′-phthalimido-1′-isopentyl)	170°	$C_{28}H_{26}N_4O_4$	11.6	11.7
4.	2-(1′-phthalimido-2′-isopentyl)	345°	$C_{28}H_{26}N_4O_4$	11.6	12.0
5.	2-(1′-methyl histidynyl 1′-phthalimido)	325°	$C_{28}H_{22}N_6O_4$	16.6	16.2
6.	2-[(1′-phthalimido) 3′-benzimidazolyl)-propyl]	235°	$C_{41}H_{33}N_7O_6$	13.6	13.9

All the melting points are uncorrected. Percent yield 50-60%.

Biological Activity

Antioestrongenic activity :

The study was conducted in nonpregnant adult

Male antifertility screening :

1-salicylamido-methyl-2-(phthalimido-ethyl),

TABLE—3 ANTIOESTROGENIC ACTIVITY OF BENZIMIDAZOLES

Compound	Dose	Duration of Treatment	Total No. Animals of	Body Weight (mg)	Mean ± S.E. Dry Uterus Weight (mg)	Dry Uterus Weight / Body Weight
Oestradiol	1 μg/100 gm	0-3	3	188.3±17.18	31.6±6.6	0.16
Oestradiol + A	1 μg/100 gm + 100 mg/kg	0-3	3	202±9.13	28.3±5.9	0.14
Oestradiol + B	1 μg/100 gm + 100 mg/kg	0-3	3	205±20.02	27.66±3.3	0.13

A 2-*p*-(3′ : 5′-dinitrophenyl carboxamide phenyl) benzimidazole
B 2-(3′ : 5′-dinitrophenyl carboxamide methyl) benzimidazole

TABLE—4 MALE ANTIFERTILITY TESTING OF 1, 2-DISUBSTITUTED-BENZIMADAZOLE

Compound	Dose mg/kg/day	No. of rats	1 BW, gms	FBW, gms	Mean±S.E. Sem. Ves., mg	V. Prost., mg	Testes, mg
Uninjected Controls	–	5	215±4	272±5	632.0±60.5	256.1±29.5	2809.8±100.4
Vehicle	–	5	225±5	289±5	582.5±76.2	306.2±16.8	2805.0±185.5
1-Salicylamido methyl-2 (Phtha-limido ethyl) benzimidazole	100.0	5	222±6	278±5	575.1±115.5	302.0±50.0	2811.6±148.0

benzimidazole was screened for antispermatogenic activity in male rats. The test compound, dissolved in propylene glycol, was administered orally at 100 mg/Kg/day once daily for five days. The autopsy was performed on the third day after the last treatment. Seminal vesicle, prostate and testes were weighed. The results are sumarized in Table 4. No significant change in organ weight and no effect on histology was noticed at the given doses.

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Structure of Two New Saponins from Stem-Bark of *Anthocephalus cadamba* Miq.

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Two new saponins (C and D) have been isolated from stem-bark of *Anthocephalus cadamba* Miq. From the results of permethylation and periodate-oxidation studies, as well as by application of Klyne's rule the structures of saponin C and saponin D are established as β-D-glucopyranosyl (1→4)-β-D-glucopyranosyl (1→3)-α-L fucopyranosyl (1→3) quinovic acid and α-L-rhamnopyranosyl (1→4) β-D-glucopyranosyl (1→2) [β-D-glucopyranosyl (1→4)] α-L-fucopyranosyl (1→3) quinovic acid respectively.

ANTHOCEPHALUS candamba Miq. (Rubiaceae) is a large deciduous tree found all over India. The stem-bark of the plant is reported[1] to be used as tonic, febrifuge astringent and also used in snake-bite. Isolation of saponin-A and saponin B from the stem-bark of the plant has already been reported[2,3]. This paper deals with the structure elucidation of saponin C and saponin D (minor constituents).

Saponin C: A new saponin $C_{48}H_{76}O_{19}$, m. p. 295° (d) $[\alpha]^{27}_{D}+4.24°$ (EtOH) which on acid hydrolysis yielded D-glucose and L-fucose in 2 : 1 molar ratio and the aglycone part was identified as quinovic acid (m.p., m.m.p,, IR, NMR, MS). Complete hydrolysis of saponin-C dimethyl ester with 7% H_2SO_4 yielded quinovic acid dimethyl ester, D-glucose and L-fucose. This showed that the sugars were linked to 3-hydroxyi of quinovic acid. Quantitative estimation of the genin (gravimetric) and sugars by Dubois method[4] showed the aglycone, D-glucose and L-fucose in the molar ratio of 1.1 : 2. 2 : 0.98. Partial hydrolysis of saponin C dimethyl ester with 1% H_2SO_4 followed by re-esterification yielded beside other products dimethyl ester of quinovic acid-α-L-fucopyranoside $C_{38}H_{60}O_9$, m.p. 240° (d), $[\alpha]_D^{27}+6.4°$ (EtOH). This glycoside on acid hydrolysis yielded dimethyl ester of quinovic acid and L-fucose in 1 : 1 molar ratio. The structure of this glycoside was established as dimethyl ester of quinovic acid-α-L-fucopyranoside by permethylation and periodate-oxidation studies. The MS of its triacetate showed fairly stable molecular ions, showing characteristic fragmentation of $\triangle^{12}$-ursene and $\triangle^{12}$-oleanene type and also 6-deoxyhexopyranoside acetate type[5]. These results showed that L-fucopyranose unit is directly linked to the aglycone. Complete methylation of dimethyl ester of the saponin was achieved by prolonged treatment with Hakomori's procedure[6]. After acid hydrolysis of the permethylate the sugar part was separated into three pure fractions by preparative paper chromatography and as identified as 2, 3, 4, 6-tetra-O-methyl-D-glucose, 2,3,6-tri-O-methyl-D-glucose and 2, 4-di-O-methyl-L-fucose. Molar ratio of the methylated sugars was determined to be 1.0 : 1.02 : 0.98 by alkaline hypoiodite method[7].

Periodate-oxidation of saponin C dimethyl ester was carried out at room temperature. Consumption of oxidant and liberation of formic acid were found to be 3.08 and 1.01 mol. respectively.

Hence the structure of saponon C dimethyl ester can be represented as D-glucopyranosyl (1→4)-D-glucopyranosyl(1→3)-L-fucopyranosyl(1→3) quinovic acid dimethyl ester.

Further support to the sequence of the sugars in the parent glycoside was obtained by subjecting the periodate-oxidised saponin Cdimethyl ester to acid hydrolysis and the hydrolysate was examined for sugars. Identification of only L-fucose supported the structure as deducted above.

The configuration of the anomeric carbon atoms of the sugars in saponin C dimethyl ester were deduced by application of Klyne's rule of molecular rotation[8] (Table 1) and was found to be α for L-fucose and β-for D-glucose. Hence the structure of saponin C was assigned as β-D-glucopyranosyl (1→4)-β-D-glucopyranosyl (1→3)-α-L-fucopyranosyl (1→3)-quinovic acid(I).

Saponin D: Saponsn D dimethyl ester (IIa) $C_{56}H_{90}O_{23}$, m.p. 302° (d) $[\alpha]^{28}_{D}-21°$ on complete hydrolysis yielded quinovic acid dimethyl ester, D-glucose, L-rhamnose and L-fucose. This established the direct linkage of sugar with 3-hydroxyl of quinovic acid. Quantitative analysis of the genin

TABLE—1 MOLECULAR ROTATION CALCULATIONS OF SAPONIN-C-DIMETHYL ESTER (IA)

Compound	[α]D	[M]D
Methyl-β-D-glucopyranoside	−34.2°	−66°
	Literature value[9]	
" " "	−34.2°	−66°
	Observed value	
For dimethyl ester of α-L-fucopyranoside of quinovic acid (III)	+6.4°	+42.2°
For compd. (Ia)	Calculated value	−89.8°
	Observed value	
For compd. (Ia)	−9.2°	−90.5°

(gravimetric) and sugars (colorimetric) showed the aglycone, D-glucose, L-rhamnose and L-fucose in the molar ratio of 1.1 : 2.2 : 1.2 : 1.09. Dimethyl ester of quinovic acid-α-L-fucopyranoside as in saponin-C was isolated from partial hydrolysis (by 1% H_2SO_4) product of saponin D. Isolation of this glycoside established the direct link of L-fucose with the aglycone. Permethylation and hydrolysis of the product yielded four pure sugar fractions which were easily identified as 2. 3, 4, 6-tetra-O-methyl-D-glucose, 2, 3, 6-tri-O-methyl-D-glucose, 2, 3, 4-tri-O-methyl-L-rhamnose and 3-O-methyl-L-fucose in the molar of 0.98 : 1.2 : 1.1 : 1.01.

On periodate oxidation the dimethyl ester of saponin-D consumed 5.11 mol of periodate with liberation of 2.08 mol. of formic acid.

Therefore, the structure of saponin-D can be represented as α-L-rhamnopyranosyl (1→4)-β-D-glucopyranosyl-(1→2) [β-D-glucopyranosyl (1→4)] α-L-fucopyranosyl (1→3) quinovic acid.

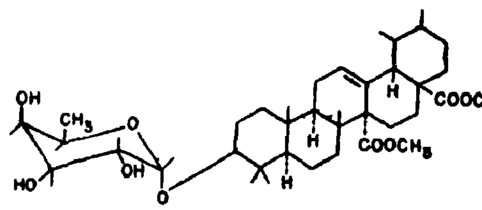
Isolation of only L-fucose from the hydrolysate of periodate-oxidised saponin-D dimethyl ester also gave additional support to the proposed structure of saponin-D.

With regard to the configuration of saponin glycosidic linkages it is a general observation that D-sugars occur with β-glycosidic linkages and L-sugars with α-glycosidic linkages[10].

The calculation of the molecular rotation (Table 2) of the dimethyl ester of saponin-D on the basis of Klyne's rule also support the type of linkages assigned. Hence the structure of saponin. D can be represent as (II).

TABLE—2 MOLECULAR ROTATION CALCULATIONS OF SAPONIN-D DIMETHYL-ESTER(IIa)

Compound	[α]D	[M]D
	−34.2°	
Methyl-β-D-glucopyranoside	Literature value[9]	−66°
" "	−34.2°	−66°
Methyl-α-L-rhamnopyranoside	−62.3°	−111°
	Observed value	
For dimethyl ester of α-L-fucopyranoside quinovic acid (III)	+ 6.4°	+42.2°
	Calculated value	
For compd. (IIa)	-	−200.8°
	Observed value	
For compd. (IIa)	− 21°	−237.3°



(III)

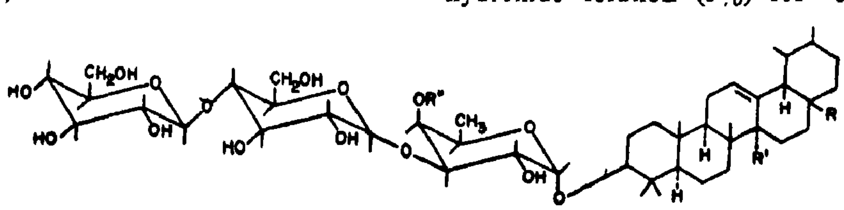
Experimental

All specific rotations are equilibrium values. All evaporations were carried out in vacuum at 35-40°. Whatman no. I paper was used for analytical paper chromatography and Whatman No. 3 MM paper for preparative chromatography.

The solvent mixture (v/v) used for partition chromatography of sugars were : A, n-butanol : acetic acid : water (4 : 1 : 5), upper layer ; B, n-butanol : pyridine : water (6 : 4 : 3) ; C, ethyl acetate : pyridine : water (8 : 2 : 1) ; D, n-butanol : ethanol : water (5 : 1 : 4), upper layer. Spray reagents were (a) aqueous saturated aniline oxalate and (b) alkaline silver nitrate solution.

Isolation of pure saponin C and D :

Air dried powdered stem-bark of *A. cadamba* was defatted with pet. ether and then successively extracted with chloroform and methanol in a Soxhlet extractor. The methanolic extract on removal of the solvent yielded a brown semi-solid material. This material was shaken with aqueous potassium hydroxide solution (5%) for one hour and then



3 2 1

I, R=R¹=COOH, R″=H
II, R=R¹=COOH, R″=D-glucopyranose, 3=α-L-rhamnopyranose, linkage bet. 2 to 1 is (1→2)
Ia, R=R¹=$COOCH_3$, R″=H
IIa, R=R¹=$COOCH_3$, R″=D-glucopyranose, 3=α-L-rhamnopyranose, linkage bet. 2 to 1 is (1→2)

filtered, residue obtained was negligible. The filtrate was acidified with hydrochloric acid when a brown precipitate was obtained. The solid was filtered, washed until acid free and dried to a brown powder. This powder was dissolved in ethanol, mixed with paper pulp dried and extracted successively with ether, ethylacetate and ethanol. Major part was collected in ethyl acetate fraction. The material was dissolved in minimum vol. of methanol and poured into a large vol. of ether. The brown solid was collected and the process was repeated until a white powder was obtained. This material was chromatographed on silica gel and saponin C and D were eluted with chloroform : methanol 95 : 5 and 92 : 8 respectively. The pure saponin C (I) and D (II) were crystallised from chloroform-methanol-ether mixture having m. p. 295° (d) $[a]_D^{27}$ +4.24° (EtOH) and m. p. 312° (d) $[\alpha]_D^{27}$ +8.4° (EtOH) respectively.

Dimethyl esters of saponins: Each saponins (500 mg) in 800 ml of methanol was treated with excess of an ethereal solution of diazomethane. The products were purified by column chromatography on silica gel. Dimethyl ester of saponin C (Ia) was crystallised from chloroform : methanol, m.p. 290-91° (d) $[a]_D^{28}$ −9.2° (EtOH). Found : C, 60.42 ; H, 8.21%, $C_{50}H_{80}O_{19}$ requires C, 60 97 ; H, 8.13) : Dimethyl ester of saponin. D (IIa) was crystallised in micro needles from methanol-chloroform, m. p. 302° (d), $[\alpha]_D^{28}$ −21° (EtOH). (Found : C, 60.1 ; H, 7.8, $C_{56}H_{90}O_{23}$ requires C, 59.4 ; H, 7.9%).

Identification of aglycone and sugars: Hydrolysis of Ia and IIa with H_2SO_4 (7%), yielded the genin as needles from methanol, m.p. 175-76°, $[\alpha]_D^{27}$ +121.1° (EtOH), and identified as dimethyl ester of quinovic acid (m. p., m m.p., IR, NMR, MS). The sugars in aqueous portion were identified as D-glucose and L-fucose in case of Ia and D-glucose, L-rhamnose and L-fucose in case of IIa (solvent systems, A, B and C).

Partial hydrolysis of Ia and IIa: 400 mg of each was refluxed with 50 ml of 1% H_2SO_4 in methanol for one hr and the product isolated was treated with excess of ethereal diazomethane and chromatographed over silica gel. Benzene eluted dimethyl ester of quinovic acid and chloroform : methanol (99 : 1) eluted dimethyl ester of quinovic acid-α-L-fucopyranoside(III), crystallised from methanol-ether, m.p. 240° (d) $[\alpha]_D^{27}$ +6.4° (EtOH) (Found : C. 70.1 ; H, 9.4 ; $C_{38}H_{60}O_9$ requires C, 69.1 ; H. 9.1%). Permethylation of III and hydrolysis yielded 2, 3, 4-tri-O-methyl-α-L-fucopyranoside syrup, $[\alpha]_D^{27}$ −127° (H_2O) (Lit.[11], m.p. 36°, $[\alpha]_D$ − 128° (H_2O).

On periodate oxidation it consumed 2.1 mols. of periodate with liberation of 1.09 mol of formic acid. Mass spectra of triacetate yielded mol. ion at m/e 785 M+ and also peaks at m/e 273 and 111 which are characteristic of acetates of 6-deoxyhexopyranoside[5].

Permethylation (Hakomoris method[6]) and hydrolysis of Ia and IIa: 50% sodium hydride dispersion in oil (ca. 120 mg) was suspended in dimethyl sulphoxide (12 ml) and kept in an oil bath at 80° for one hour. A solution of saponin-dimethyl ester (70 mg) in dimethyl sulphoxide (2.5 ml) was then added gradually and the mixture was kept at 80° for one hour with constant stirring. It was cooled in ice and methyl iodide (1.5 ml) was added in drops. The fully methylated product isolated in the usual way (syrup) showed no absorption band in the region of 3500-3600 cm^{-1} in IR. The fully methylated product was hydrolysed with N-H_2SO_4 for 10 hrs on a boiling water bath. The hydrolysate was neutralised with $BaCO_3$, filtered, deionised and evaporated to a syrup. The syrup was separated into three and four pure fractions in case of Ia and IIa respectively by preparative paper chromatography. In case of Ia, the methylated sugars were identified as 2, 3, 4, 6-tetra-O-methyl-D glucose, m.p. 92-93° $[\alpha]_D^{28}$ +81° (H_2O). (Lit[12]. m.p. 96° $[\alpha]_D$+84°), 2, 3, 6-tri-O-methyl. D-glucose m. p. 120-21°, $[\alpha]_D^{28}$ +68.9° (H_2O) (Lit.[13] m.p. 121-23°, $[\alpha]_D$+70°) and 2,4-di-O-methyl-L-fucose, m.p. 129-30°, $[\alpha]_D^{28}$ −84° H_2O, (Lit[14]. m.p. 131-32° $[\alpha]_D$−85°). Molar ratio of the methylated sugars was found to be 1.0 : 1.02 : 0.98 by alkaline hypoiodite method[7].

In case of IIa, the methylated sugars were identified as 2,3 4,6-tetra-O-methyl-D-glucose and 2, 3, 6-tri-O-methyl-glucose (m.p. and $[\alpha]$D values are as in the above), 2,3,4-tri-O-methyl-L-rhamnose, syrup, $[\alpha]_D^{28}$ +24.1° (H_2O) (Lit. 15a, 15b syrup $[\alpha]_D$. +26°) and 3-O-methyl-L-fucose. syrup $[\alpha]_D^{28}$ − 92.8° (H_2O) (Lit[16] syrup, $[\alpha]_D$−94°). Methylated sugars were also compared with authentic samples. Molar ratio of methylated sugars in case of IIa was determined to be 0.98 : 1.2 : 1.1 : 1.01.

Periodate-oxidation studies on dimethyl ester of saponins (C and D) were carried out with 0.1 *M* sodium metaperiodate solution. Consumption of the oxidant was determined spectrophotometrically[17] and was found to become constant in 30 hrs and 40 hrs corresponding to 3.08 and 5.11 mols for Ia and IIa respectively. The liberation of formic acid were estimated in the usual way[18] and become constant in the same time corresponding to 1.01 and 2.08 mol for Ia and IIa respectively.

Periodate-oxidised Ia and IIa were hydrolysed

with N-H_2SO_4 and sugars were identified from hydrolysates. Only L-fucose was detected in both the cases.

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Photolytic Chlorination of Aromatic Nitro Disulphides

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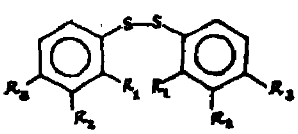
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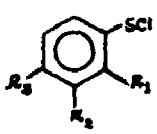
Photolytic chlorination of bis(2-nitrophenyl) disulphide (Ia), *bis*(2, 4-dinitrophenyl) disulphide (Ib) and bis(4-nitrophenyl) disulphide (Ic) in carbontetrachloride resulted in the formation of the corresponding nitrobenzenesulphenyl chloride (IIa-c) in good yields. *bis*(3-nitrophenyl) disulphide (Id) under these conditions did not afford the corresponding sulphenyl chloride. Ia and Ib on photolytic chlorination in aqueous acetic acid afforded 2-aminobenzenesulphonic acid (Va) and 2-amino-4-nitrobenzenesulphonic acid (Vb) respectively. Ic under these conditions gave 4-nitrobenzenesulphenic acid (VI).

DISULPHIDES are known to dissociate homolytically at elevated temperature and under photolytic conditions[1-3]. The ability of an *ortho*-nitro group to transfer its oxygen(s) to an adjacent group under photochemical conditions is known and has been reviewed[4]. Our interest in the photochemical interactions between a sulphur likage and an *ortho*-nitro group[5,6] prompted an investigation of the photochemical chlorination of aromatic disulphides bearing an *ortho*- nitro substituent.

When a stream of dry chlorine was passed into a suspension of *bis*(2-nitrophenyl) disulphide (I*a*) in carbon tetrachloride, while the suspension being irradiated with a Philips HPK 125W mercury-quartz lamp in a Hanovia photochemical reactor, the disulphide gradually went into solution. The reaction was complete in 30 minutes and work-up under anhydrous conditions afforded 2-nitrobenzenesulphenyl chloride (II*a*). Similar reaction of *bis*(2,4-dinitrophenyl) disulphide (I*b*) and *bis*(4-nitrophenyl) disulphide (I*c*) afforded 2,4-dinitrobenzenesulphenyl chloride (II*b*) and 4-nitrobenzenesulphenyl chloride (II*c*) respectively. *Bis* (3-nitrohenyl) disulphide (I*d*) under these conditions gave no sulphenyl chloride, but only decomposed resinuous products which could not be characterised.



I



II

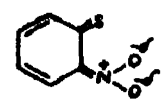
a. $R_1 = NO_2$; $R_2 = H$; $R_3 = H$ — *a.* $R_1 = NO_2$; $R_2 = R_3 = H$

b. $R_1 = NO_2$; $R_2 = H$; $R_3 = NO_2$ — *b.* $R_1 = R_3 = NO_2$; $R_2 = H$

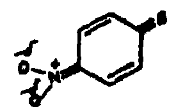
c. $R_1 = H$; $R_2 = H$ $R_3 = NO_2$ — *c.* $R_3 = NO_2$; $R_1 = R_2 = H$

d. $R_1 = H$; $R_2 = NO_2$; $R_3 = H$

The ease of chlorination of aromatic disulphides containing *o*-and *p*-nitro substituents can be ascribed to the favoured formation of *o*-nitrophenyl thiyl and *p*-nitrophenyl thiyl radicals. The formation of these radicals and hence the homolysis of the disulphide linkage is favoured due to the resonance interaction involving the nitro group at *o*- and *p*- positions (canonical forms III & IV).

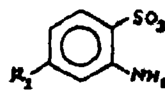


III

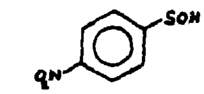


IV

Recent investigation by one of these authors[5] has shown that *o*-nitrobenzenesulphenyl chloride undergoes an intenal photo-redox reaction in aqueous acetic acid forming 2-aminobenzenesulphonic acid (V*a*). Therefore it was thought of interest to carry out the photolytic chlorination of the disulphides in aqueous acid. Thus, *bis*(2-nitrophenyl) disulphide (I*a*) and *bis*(2,4-dinitrophenyl) disulphide (I*b*) on photolytic chlorination in aqueous acetic acid yielded 2-aminobenzenesulphonic acid (V*a*) and 4-nitro-2-aminobenzenesulphonic acid (V*b*) respectively. *Bis*-(4-nitrophenyl) disulphide (I*c*) under these conditions affoaded 4-nitrobenzenesulphenic acid (VI).



V



VI

a. $R_1 = H$

b. $R_1 = NO_2$

The formation of the 2-aminobenzenesulphonic acids is evidently through the intermediacy of the 2-nitrobenzenesulphenyl chlorides. This then follows the reported internal photo-redox reaction to form the 2-amino compounds. This view is supported by the non-formation of the amino compound in the case of the 4-nitro compound (I*c*) in which the interaction involving the neighbouring nitro group is impossible.

Experimental

Melting points are uncorrected. Irradiations were carried out with a Philips HPK 125W high-pressure mercury-quartz lamp in a Hanovia one litre photochemical reactor. The lamp was surrounded by cylindrical water-jacket made of quartz which in turn was surrounded by a jacket containing the solution to be irradiated.

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Preparation of disulphides (I): The nitrodisulphides (Table-1) were prepared by refluxing the corresponding nitrochlorobenzene (2 equivalents) with sodium disulphide (1 equivalents) in ethanol[7].

TABLE—1

Disulphide	m.p., °C	Nitrogen per cent*
Bis (2-nitrophenyl disulphide(Ia)	197	9.6(9.9)
Bis (2, 4-dinitrophenyl) disulphide (Ib)	215	14 0(14.1)
Bis (4-nitrophenyl) disulphide(Ic)	135	9.8(9.9)
Bis (3-nitrophenyl) disulphide(Id)	188	9.5(9.9)

*Calculated values in parantheses

Photolytic chlorination of the disulphides in CCl_4: Details of a typical reaction are as follows: *bis*(2-nitrophenyl) disulphide (I*a*. 5g) was suspended in CCl_4 (500ml) in the photochemical reactor. A crystal of iodine was added to this and a stream of dry chlorine was passed into the suspension while the solution being irradiated with the mercury-quartz lamp. The disulphide gradually dissolved. After 30 minutes the resulting yellow solution was concentrated to 50ml by distillation of the solvent on a waterbath. The solution was cooled in ice, filtered the yellow needles (4.5g, 90 per cent) of 2-nitrobenesulphenyl chloride (II*a*), m.p., 73°C (lit[8]. 73°); found: C, 38.1; H,2.0; N,7.7 per cent; Calcd. for: $C_6H_4NO_2SCl$: C,38.1; H,2.1; N,7.9 per cent.

The other nitrobenzenesulphenyl chlorides were also prepared similarly.

TABLE—2

Suplhenyl chloride	m.p., °C	Percentages* C H N
2-Nitrobenzene-sulphenyl chloride (IIa)	73	38.1(38.1), 2(2.1), 7.7(79.)
2, 4-dinitrobenzene-sulphenyl chloride (IIIb)	97	30.5(30.8), 1.3(1.3), 11.7(12)
4-Nitrobenzene-sulphenyl chloride (IIc)	158	37.8(38.1), 2.0(2.1), 7.6(79.)

*Calculated values in parantheses

Photolytic chlorination in aqueous acetic acid: I*a* (5g) was suspended in acetic acid (800ml) containing 50 ml of water in the photoreactor. A stream of dry chlorine was passed into the suspension while it being irradiated with the mercury-quartz lamp. The disulphide gradually dissolved and after about 10 hrs a crystalline precipitate began to appear. After 20 hrs of irradiation the solvent was distilled off and the residue (3.7g, 75%) on crystallisation from hot waer afforded orthanilic acid or 2-amintobenzenesulphonic acid (V*a*) as colourless flakes. Similar reaction of I*b* afforded 4-nitro-2-aminobenzenesulphonic acid (V*b*) in 65 per cent yield. I*c* under these conditions yielded 4-nitrobenzene-sulphenic acid (VI) m.p.. 197°; Found: C 42.2; H, 2.8; N, 8.3%; Calcd. for $C_6H_5NO_3S$: C, 42.6; H, 2.9; N, 8.3%. The same compound (VI) was obtained on treatment of 4-nitrobenzenesulphenyl chloride with aqueous acetic acid.

Acknowledgement

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Synthesis of Some Enaminonitriles

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Several substituted cyanoacetamides were prepared which were converted into ∝-cyano-∝, ∝-bis(β-cyanoethyl) (R) amides. A series of products obtained by cyanoethylation were subjected to Thorpe-Ziegler cyclization. The intermolecular condensation takes place and cyclic enaminonitriles are formed. They have been characterized by infrared and ultraviolet spectroscopy.

IN an earlier communications, the cyanoethylation reaction has been successfully applied towards synthesizing insecticides, pressor active compounds and coordination compounds. It was worthwhile to study that such compounds can also undergo Thorpe-Ziegler cyclization. It is with this idea that several cyanoethylated cyanoacetanilides, substituted cyanoacetanilides, cyanoacetamides and malondibenzylamides have been synthesized and then cyclized by the route outlined below.

Pimelonitrile is readily cyclized with sodium hydride to 4-amino-2-cyanocyclohexene and substituted pimetonitriles react similarly[1]. The Thorpe-Ziegler cyclization is equally applicable to the synthesis of spiro derivatives of 1-amino-2-cyanocyclohexane. Thus *bis*-cyanoethylation product of fluorene[2] is also cyclized.

Hammer and Hines[3] have studied the Thorpe-Ziegler reaction in case of five membered ringe.

Experimental

Cyanoacet-methylamide : Ethylcyanoacetate (5 g, 0.044 mol), 25% methylamine solution (6.48 g. 0.044 mol) and 0.02 g of sodium hydroxide were taken in a round bottomed flask. The mixture was shaken to make it homogeneous. It was then heated on a water bath for two hours and cooled. The solid mass thus separated, was recrystallized from benzene. The cyanoacetamides were characterized by their sharp melting points and analysis (Table 1).

∝, ∝-bis (β-cyanoethyl) cyanoacet-methylamide : To a stirred solution of cyanoacetmethylamide (2g. 0.02 mol) dioxan and Triton B (1 g) was added acrylonitrile (2.1 g, 0.04 mol), dropwise. Stirring was continued for four hours. The solution was neutralized with dil. HCl. The solid mass was recrystallized from alcohol. The cyanoethylated cyanoacetamides were characterized by their sharp melting points and analysis (Table 2).

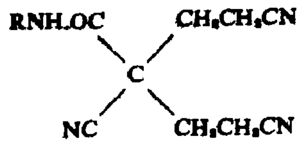
1-Amnio, 2, 4 dicyano, 4 methylacetamido cyclohexane : 2.5 g of sodium slurry in dimethyl sulphoxide was added to a mixture of ∝, ∝-*bis*-(β-cyanoethyl) cyanoacetmethylamide (4g, 0.02 mol). It was then heated on oil bath at 90-100° for two hours. After neutralizing with dil. acetic acid. It was poured in ice water and then extracted with ethyl acetate. The solid mas was crystallized from alcohol. These acetamidocyclohexenes were characterised by their sharp melting points and analyses (Table 3).

Discussion of Experimental Results : The Thorpe-Ziegler cyclization carried on nitriles described in the experimental part, gave cyclic products in very good

TABLE—1 ALKYL AND ARYL SUBSTITUTED CYANOACETAMIDES.

Sl. no.	Compound	Molecular Formula	M.P. °C	Yields %	Percentage of Nitrogen Found	Calcd.
1.	Cyanoacet-methylamide	$C_4H_6N_2O$	101	40.90	28.60	28.57
2.	Cyanoacet-ethylamide	$C_5H_8N_2O$	74	50.50	25.10	25.00
3.	Cyanoacet-propylamide	$C_6H_{10}N_2O$	45-46	43 80	22.15	22.20
4.	Cyanoacet-isopropylamide	$C_6H_{10}N_2O$	65	43.80	22 40	22.20
5.	Cyanoacet-*n*-butylamide	$C_7H_{12}N_2O$	73	64.50	20.21	20.00
6.	Cyanoacet-*o*-toluidide	$C_{10}H_{10}N_2O$	125	75.40	15.98	16.09
7.	Cyanoacet-benzylamide	$C_{10}H_{10}N_2O$	120	76.50	16.12	16.09
8.	Cyanoacet-naphthylamide	$C_{13}H_{10}N_2O$	175	87.90	13.50	13.30
9.	Cyanoacet-naphthylamide	$C_{13}H_{10}N_2O$	174	76.90	13.36	13.33

TABLE—2 ∝,∝-*bis*-(β-CYANOETHYL)ACET (R) AMIDE



Sl. no.	Compound	Molecular Formula	M.P. °C	Yields %	Percentage of Nitrogen Found	Calcd.
1.	∝, ∝-*bis*-(β-cyanoethyl)-cyanoacet-methylamide	$C_{10}H_{12}N_4O$	90	50.00	27.50	27.45
2.	∝, ∝-*bis*-(β-cyanoethyl)-cyanoacet-ethylamide	$C_{11}H_{14}N_4O$	62	66.60	25.62	25.69
3.	∝, ∝-bis-(β-cyanoethyl)-cyanoacet-propylamide	$C_{12}H_{16}N_4O$	48	72.70	24.20	24.13
4.	∝, ∝-*bis*-(β-cyanoethyl)-cyanoacet-isopropylamide	$C_{12}H_{16}N_4O$	86-87	65.20	24.12	24.13
5.	∝, ∝-*bis*-(β-cyanoethyl)-cyanoacet-butylamide	$C_{13}H_{18}N_4O$	118	71.40	22.80	22.76
6.	∝, ∝-*bis*-(β-cyanoethyl)-cyanoacet-*o*-toluidide	$C_{16}H_{16}N_4O$	85	75.00	20.01	20.00
7.	∝, ∝-*bis*-(β-cyanoethyl)-cyanoacet-benzylamide	$C_{16}H_{16}N_4O$	84-85	80.00	19.98	20.00
8.	∝, ∝-*bis*-(β-cyanoethyl)-cyanoacet-naphthylamide	$C_{19}H_{16}N_4O$	78	74.70	17.80	17.72
9.	∝, ∝-*bis*-(β-cyanoethyl)-cyanoacet-naphthylamide	$C_{19}H_{16}N_4O$	89	66.60	17.68	17.72

The following compounds have been reported in earlier communications :
∝, cyano, ∝, ∝-*bis*-(β cyanoethyl) acetanilide, and ∝, ∝-*bis*-(β-∝-cyano, ∝, ∝-*bis*-(β-cyanoethyl)-*p*-chloracetanilide cyanoethyl) malondibenzylamide.

TABLE—3 1, AMINO DERIVATIVE OF SUBSTITUTED CYCLOHEXENES

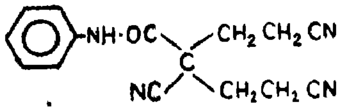
Sl. no.	Compound	Molecular formula	Melting point °C	Yield	% Carbon Calcd.	Found	% Hydrogen Calcd.	Found	% Nitrogen Calcd.	Found
1.	1, Amino, 2, 4 dicyano, 4 acetanilido cyclohexene	$C_{18}H_{14}N_4O$	120	87.56	7.66	67.8	5.02	5.13	21.05	21.24
2.	1, Amino, 2, 4 dicyano-4-*p*-chloro acetanilido cyclohexene	$C_{18}H_{13}O_4NCl$	140	80	59.90	60	4.32	4.33	18.63	18.66
3.	1, Amino, 2, 4-dicyano-4-methylacetamido cyclohexene	$C_{10}H_{12}N_4O$	65	71.4	58.82	58.88	5.88	5.82	27.45	27.48
4.	1, Amino, 2, 4-dicyano, 4 ethylacetamido cyclohexene	$C_{11}H_{14}N_4O$	75.76	94.1	60.55	60.6	6.42	6.44	28.68	28.66
5.	1, Amino, 2, 4-dicyano, 4-*o*-toluidocyclohexene	$C_{16}H_{16}N_4O$	100	94.5	68.57	68.59	5.71	5.73	20	20.1
6.	1, Amino, 2, 4-dicyano, 4 benzylamido cyclohexene	$C_{16}H_{16}N_4O$	98	85.7	68.57	68.56	5.71	5.7	20	02.2
7.	1, Amino, 2, cyano, 4, 4-dibenzylamido cyclohexene	$C_{23}H_{24}N_4O$	120	90	71.13	71.2	6.18	6.19	14,43	14.47

yields and the course of the reaction may be shown as below.

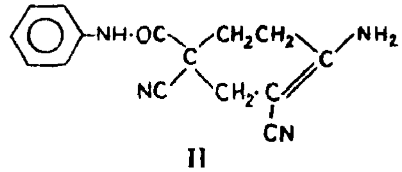
The other nitriles also reacted analogously. The infra red and ultra violet spectra of all the compounds (Tables 4 & 5) are consistent with the proposed structure (II).

Baldwin[6] and Karle's[5] study of I. R. and U.V. spectra of enaminonitriles provide additional support for the structure (II).

All the enaminonitriles except 1-amino-2-cyano, 4,4 dibenzylamidocyclohexene showed two peaks for the -C≡N group, one appearing for conjugated nitrile group. From the Table 3 one can observe that it appears usually at 2190 cm^{-1} which indicates a rather unusual conjugated nitrile. In the table 3 enaminonitrile structures for the compounds have usually low-C≡N stretching frequencies. It is reported by Ketson and Griffith[6] that 2218 cm^{-1} is the lowest frequency for an ∝, β-unsaturated alkylnitrile.



I



II

TABLE—4 INFRARED SPECTRA OF SUBSTITUTED CYCLOHEXENE

Sl. no.	Compound	NH frequencies in cm^{-1}	-C≡N stretching frequency in cm^{-1}	C═C frequencies in cm^{-1}
1.	Amino, 2, 4-dicyano, 4 acetanilido cyclohexene	3510,3450 1650	2190,2250	1620
2.	1, Amino, 2, 4-dicyano-4-p-chloro acetanilido cyclohexene	3450,3200 1645	2191,2250	1580
3.	1, Amino, 2, 4 dicyano, 4, methyl-acetamido cyclchexene	3450,3175 1637	2200,2252	1592
4.	1, Amino, 2, 4-dicyano, 4 ethyl-acetamido cyclohexene	3435,3137 1650	2198,2250	1608
5.	1, Amino, 2, 4-dicyano, 4-o-toluido cyclohexene	3500,3401 1625	2200,2260	1580
6.	1, Amino, 2, 4-dicyano, 4-benzylamido cyclohexene	3435,3130 1650	2202,2258	1580
7.	1, Amino, 2 cyano, 4, 4 dibenzylamido cyclohexene	3450,3150 1650	2190	1585

TABLE—5 ULTRAVIOLET SPECTRA OF SUBSTITUTED CYCLOHEXENES IN METHANOL

Sl. no.	Name of compound	λ_{max}	λ_{max}
1.	1, Amino, 2, 4-dicyano, 4 acetanilido cyclohexene	260	14,572
2.	1, Amino, 2, 4-dicyano, 4-p-chloro acetanilido cyclohexene	262	18,576
3.	1, Amino, 2, 4-dicyano, 4-methyl-acetatamido cyclohexene	264	13,000
4.	1, Amino, 2, 4-dicyano, 4, methyl-acetamido cyclohexene	265	14,000
5.	1, Amino, 2, 4-dicyano, 4-o-toluido cyclohexene	260	13,230
6.	1, Amino, 2, 4-dicyano, 4-benzylamido cyclohexene	260	10,990
7.	1, Amino, 2-cyano, 4, 4, di benzylamidocyclohexene	263	22,155

The values of the nitrile frequencies in Table 3 have been depressed by 17-38 cm^{-1} below the 2218 cm^{-1} and occurs usually at 2190 cm^{-1} responsible for further shift of the nitrile frequency. Baldwin[4] proposed that this abnormal shift is due to increased interaction between the p-electrons on the nitrogen atom and the π electrons of the double bond and in turn with the π electrons of the nitrile group itself.

Further support for the enaminonitrile structure (II) is the appearance of two bands in the >NH stretching region i.e. at 3510^{-1} and 3450 cm^{-1}. This is compatible only with a primary amino group. If an amino group were present, only one band should appear in this region[8]. The olefinic linkage is observed at 1620 cm^{-1}.

Therefore this abnormally large shift must be due to same influence other than simple conjugation with α, β-double bond. It has been stated by Hammer and Hines[7] that the amino group was presumably

The ultra violet spectra of all the compounds listed in Table 5 offer further evidence for the existence of an unusual conjugated nitrile group, since there is a major absorption at 263-265 μ. The E_{max} is from 10,000 to 22,000 which is also very intense and is also due to the amino group which has a powerful effect on UV absorption of these conjugated nitrile groups[5].

Acknowledgement

The authors wish to thank the Head of Chemistry Department, Lucknow University for constant interest in the work and Dr. Nitya Anand, Director, Central Drug Research Institute, Lucknow for providing facilities for microanalysis, infra red and ultra violet absorption measurements.

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Phytosterol Derivatives as Potential Antitumour Agents

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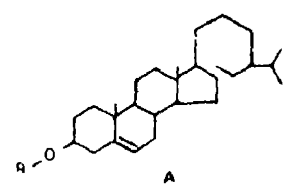
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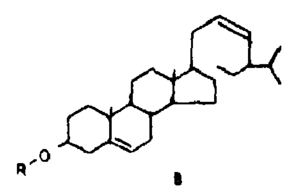
Several substituted urethane derivatives of β-sitosterol and stigmasterol as also their lauroyl esters were prepared as potential anti-tumour agents. On biological testing, none of the compounds, however, showed any activity.

β-SITOSTEROL, ('A',R,=H), is a common phytosterol occurring in plants. In the antitumour screening of plant products, β-sitosterol appeared frequently as a constituent active against Walker carcinosarcoma 256. It has been shown to have some activity against Lewis Lung carcinoma and Murphy Sturm lymphosarcoma and marginal activity against Adinocarcinoma. Further, some more soluble derivatives of β-sitosterol viz. the hemisuccinate and carboxymethylthiohemisuccinate were prepared. Though these derivatives had better solubility than the *original* sterol and activity against Walker carcinosarcoma was retained, the therapeutic indices were not sufficiently high.[1] A survey of literatures showed that no other 'simple' sterol (i.e. excluding those with a lactone function) possesses *in vivo* or *in vitro* antitumour activity with the exception of estrone. Because β-sitosterol can be obtained from natural sources, we wanted to utilise it by converting into some suitable derivatives which might have better therapeutic indices.

Urethane and its derivatives have profound carcinostatic activity[2-4]. We, therefore, thought it desirable to introduce the urethane moiety in β-sitosterol as its substituted esters. Moreover, finding that certain fatty acids and their esters have significant carcinostatic activity[5], the lauroyl ester of the sterol was prepared. Along with these, two derivatives of another plant sterol, i.e., stigmasterol (B,R = H) were also prepared. This paper describes the preparation of the sterol derivatives and the studies on their antitumour activities.



A



B

R	*R*
I = Ph-HN-CO-	V = Ph-NH-CO
II = *p*Cl-Ph-NH-CO-	VI = CH_3-$(CH_2)_{10}$-CO
III = C_2H_5-HN-CS-	
IV = $CH_3(CH_2)_{10}$-CO	

Chemistry: β-Sitosterol extracted from soyabeans was purchased from Sigma Chemical Co., U.S.A., The product was further purified by column chromatography through silica gel to obtain a homogeneous pure sample of β-sitosterol which was used in subsequent experiments. Stigmasterol, purchased from Sigma Chemical Co., was also similarly purified and used. In the preparation of N-phenyl and N-*p*-Chlorophenyl urethanes, the sterols were refluxed with respective isocyanates in benzene for different lengths of time. The rest of the compounds were prepared by direct refluxing of the sterol in the reagents, thereby eliminating the use of solvent as a medium. The crude products were purified by column chromatography through silica gel and crystallised from suitable solvents. The compounds were characterised by their elemental analyses, infra red and ultraviolet spectra. The physical constants of the compounds are listed in Table-1.

TABLE—1

Compound	Melting point °C	% Yield	Mol. Formula	Carbon %: Calcd	Carbon %: Found	Analytical Hydrogen %: Calcd	Analytical Hydrogen %: Found	Nitrogen % Calcd	Nitrogen % Found	λmax, nm	Specific Rotation $[\alpha]_D^{30}$ (In $CHCl_3$)
I	183-85°	61.06	$C_{36}H_{55}O_2N$	81.0	80.88	10.38	10.29	2.62	2.60	232	-26°
II	167.5°	77	$C_{36}H_{54}O_2NCl$	76.12	76.6	9.51	9.93	2.46	2.44	244	-28.57°
III	217-218°	42.4	$C_{32}H_{55}ONS$	76.64	77.1	10.98	12.7	2.794	2.84	246	-42°
IV	82-83°	66 8	$C_{41}H_{72}O_2$	82.55	83.1	12.08	12.5	-	-	210	-11.9°
V	193-96°	64.2	$C_{36}H_{53}O_2N$	81.30	80.71	10.05	10.49	2.63	2.62	235	-42.8°
VI	93-95°	41.7	$C_{41}H_{70}O_2$	82.81	82.3	11.7	12.2	-	-	210	-31°

Exaperimental

The melting points were determined in open capillary tubes and are uncorrected. The ultraviolet spectra were measured in methanol solution with a Hilger spctrophotometer. The optical rotation was measured in chloroform in Hilger Watt's Polarimeter. The samples were dried *in vacuo* over phosphorus pentoxide for microanalysis. The elemental analyses and infrared spectra were determined at Central Drug Research Institute, Lucknow.

N-Phenyl β-sitosteryl urethane (*I*). Phenyl isocyanate (17 ml., ~100m. moles) was added gradually to β-sitosterol (20.7g ; 50 m. moles) dissolved in 50 ml. dry benzene and the solution refluxed on a water bath for 10 hours. On cooling, the product deposited as solid, was filtered and washed with a little benzene and dried. The crude product dissolved in benzene was chromatographed through a column of silica gel (340 g). The fraction obtained in the benzene-petroleum ether (1: 1) eluent was twice crystallised from a mixture of the same solvents.

M.P., 183-185° ; yield, 8.141g. ν in cm^{-1} : 2800 $(CH_2)_n$; 1730 (-N-$\overset{\text{O}}{\overset{\|}{\text{C}}}$-O) ; 1600 (aromatic) ; 1430 (C=C-H, δ -CH in plane) ; 1370-($C\text{-}CH_3$) ; 1028 (eq. acyl group).

N-p-Chlorophenyl β-sitosteryl urethane (*II*). β-Sitosterol (4.14g. ; 10 m. moles). was dissolved in 25 ml. hot benzene and *p*-chlorophenyl isocyanate (3.07g ; 20 m. moles) in 5ml. benzene was added to it and the mixture refluxed on a water bath for 10 hrs. The solid, separated on cooling was filtered. The product was then chromatographed through a column of silica gel (200g.). The colourless solid obtained from the petroleum ether eluate on crystallisation from benzene yielded II. M. P. 167.5°, yield 4.35g. ν in cm^{-1} : 2941, 2857 $(CH_2)_n$; 1724 (N-$\overset{\text{O}}{\overset{\|}{\text{C}}}$-O-) ; 1410 (-C=C-H, δ CH in plane) ; 1379 ($C\text{-}CH_3$) ; 1020-(eq.acyl gr.).

N-Ethyl β-Sitosteryl thiourethane (*III*) : β-Sitosterol (4.48g) ~11m. moles), dissolved in a large excess of ethyl isothiocyanate (12 ml.) was refluxed for 50 hrs. The solid that deposited on cooling was filtered and washed with petroleum ether. The crude product, dissolved in benzene, was passed through a column of silica gel (160 g.). III was obtained in the benzene fraction and was crystallised twice with benzene. M.P. 217-218°. Yield, 3g. ν in cm^{-1} : 2941, 2857 $(CH_2)_n$; 1563 (-$\underset{\text{S}}{\underset{\|}{\text{C}}}$-N<), 1379, 1389 ($C\text{-}CH_3$) ; 1026, 1036 (eq. acyl groups).

N-Phenyl stigmasteryl urethane (*V*) : Procedure same as described in case of the compound I. Crystallisation from petroleum ether gave V, m.p. 192-195°. Yield 4.09g. ν in cm^{-1} : 2800 $(CH_2)_n$; 1707(-N-$\overset{\text{O}}{\overset{\|}{\text{C}}}$-O), 1600 (aromatic), 1430 (C=C-H, δ CH in plane) ; 1362 ($C\text{-}CH_3$) ; 1030 (eq. acyl group).

β-Sitosteryl laurate (*IV*) : 5 m. moles of β-sitosterol (2.07g) dissolved in lauroyl chloride (30 m. moles ; 6.6g) was heated on a water bath for 15 min. The reaction mixture was cooled and carefully poured on crushed ice. The solid separated was filtered and dried. The material was then extracted with petroleum ether and the extract was dried over anhydrous sodium sulphate. After concentration, the solution was passed through a column of silica gel (60g).

Elution of the column with petroleum ether gave the desired product IV, which was crystallised from benzene-methanol mixture. m. p., 82-83°, yield 2.03g. ν in cm^{-1} : 2899$(CH_2)_n$; 1750 (ester-CO-O-) ; 1380 ($C\text{-}CH_3$) ; 1032 (eq. acyl group).

Stigmasteryl laurate, (VI) : Procedure same as in case of IV. After elution through a column of silica gel, the product was crystallised from benzene ethanol mixture. M. P. 93-95° Yield : 64.2 g ν in cm^{-1} : 2857 (CH_{2n}) 1735(ester, CO-O) ; 1375—($C\text{-}CH_3$) ; 1026 (eq. acyl group).

Biological assay : All the compounds were tested against sarcoma-180 in strain A mice. Testing of compounds II, III, VI were carried out in KB cell culture, I, II and III against lymphoid leukemia L1210, and IV and VI against lymphocytic leukemia, P 388. None of the compounds, however, showed any activity to justify their development as useful drugs.

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Notes

Complexes of UCl_5 with Methyleneanthrone, Benzalanthrone and Dioxane.

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SELBIN and coworkers have synthesized and characterized UCl_5 complexes with N, P, As, Bi, O, S, Se and Te donors[1,2]. We have reported the synthesis and characterisation of UCl_5 complexes with some N and O donors[3,4,5]. In the present work we report the synthesis of UCl_5. 2B (B= methyleneanthrone, benzalanthrone and dioxane) complexes. IR, ESR and reflectance spectra and magnetic susceptibilities have been studied to characterize them.

Experimental

UCl_5 was prepared by refluxing UO_3 or UO_2Cl_2 with $SOCl_2$[4,5]. Methyleneanthrone and benzalanthrone were prepared and recrystallized as reported in literature[6,7].

UCl_5. 2B type complexes : Methyleneanthrone, benzalanthrone and dioxane were dissolved in ice cooled $SOCl_2$ and then added to an ice cooled solution of UCl_5 in $SOCl_2$ in 2 : 1 molar ratio. On the addition of petroleum ether dark brown solids in the case of methyleneanthrone and benzalanthrone and deep yellow complex in the case of dioxane got precipitated. These complexes were washed with dry petroleum ether and dried in vacuum.

The analytical results are given in Table 1.

TABLE—1 UCl_5 COMPLEXES WITH OXYGEN BASES

Complex	Analytical results					
	Found (%)			Required (%)		
	Uranium	Chloride	Anthrone	Uranium	Chloride	Anthrone
UCl_5. 2-methyleneanthrone	28.61	21.20	50.25	28.78	21.43	49.80
UCl_5. 2-benzalanthrone	24.52	18.00	57.15	24.30	18.10	57.60
UCl_5. 2-dioxane	40.05	30.12	-	40.26	29.98	-

Results and Discussion

UCl_5. 2B and UCl_5. 3 dioxane complexes are stable in dry and inert atmosphere and disproportionate into U(IV) and U(VI) in the presence of moisture. These complexes are insoluble in common organic solvents but disproportionate in U(IV) and (VI) in polar solvents. Reflectance and ESR spectra have been used to make the distinction of U(V) from an equimolar mixture of U(IV) and U(VI). Bagnall and coworkers[8] report that there is a characteristic peak for U(V) in the range 600-900 nm. We have already reported the reflectance spectra of UCl_5 complexes with some nitrogen[4] and oxygen[5] donor ligands which record a characteristic peak in the above mentioned range. In the present paper reflectance spectra of UCl_5. 2 methyleneanthrone, UCl_5. 2 benzalanthrone and UCl_5. 2 dioxane have been studied which record strong absorption peaks at 855, 865 and 860 nm respectively.

ESR spectra of UCl_5.2-methyleneanthrone, UCl_5. 2-benzalanthrone, UCl_5.2-dioxane and UCl_5. 3 dioxane produce broad signals at ~5925, 5960, 6000 and 5950 Gauss at 80°K and 'g' values are 1.12, 1.13, 1.13 and 1.12 respectively. These 'g' values are comparable to the average 'g' value of ~1.1 already reported[4,5,9] but in contrast to 'g' values of ~2.0 reported by Selbin et al[1,2]. From ESR spectra of UCl_5 complexes it can be inferred that 5f' electron in U(V) is not heavily delocalized into the π-antibonding molecular orbitals of the organic ligands.

In the IR spectra of UCl_5.2-methyleneanthrone and UCl_5.2-benzalanthrone γ(C=O) from 1650^5 cm^{-1} is lowered to 1590 and 1580 cm^{-1} respectively indicating that oxygen atom of these anthrones coordinates to uranium atom of UCl_5. The probable coordination number of uranium is seven in these complexes. IR spectra of UCl_5. 2-dioxane, UCl_5. 3-dioxane and dioxane resemble each other very closely. Apart from some intensity changes, only noticeable differences are the slightly higher or lower frequencies of some absorption bands for the complexes than for dioxane. The similarity of the spectra of the complexes and the free ligand have also been previously observed for $SbCl_5.C_4H_8O_2$ and $MCl_2.C_4H_8O_2$ ($M = Hg^{2+}, Cd^{2+}, Cu^{2+}$ and Ni^{2+})[10-12]. Since there is good evidence that dioxane consists of molecules in the chair configuration in both liquid and solid state, it is probable that the structure of dioxane in these complexes has also chair configuration. Therefore, polymeric structures with chains of metal ions linked through

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dioxane molecules may be proposed for these complexes.

Magnetic susceptibilities of UCl_4 complexes have been studied by various workers[1-5,8]. Magnetic susceptibilities of UCl_4. 2-methyleneanthrone, UCl_5. 2-benzalanthrone and UCl_4. 2-dioxane have been measured at room temperature only giving μ_{eff} values of 1.81, 1.75, and 1.71 B.M. respectively. These values are very close to the spin value only.

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Preparation of 4'-Amino-3-carboxy-6-methoxy-diphenyl Sulphide and its Derivatives

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3-Mercaptoanisic acid has been obtained by the reduction of 3-chlorosulphonylanisic acid[1] by Gattermann's method[2] or by hydrolysis of the xanthate derivative of 3-aminoanisic acid[3]. We have now obtained this compound in 81% yield by reducing 3-chlorosulphonylanisic acid with stannous chloride and hydrochloric acid. It was characterised through some new derivatives, *viz*. disulphide, ethyl thioether and thioglycollic acid. We also record here the preparation of hitherto unreported 3-carboxy-6-methoxy-4'-nitrodiphenyl sulphide by condensation of the mercaptan with 4-chloronitrobenzene and its reduction product 4'-amino-3-carboxy-6-methoxy-diphenyl sulphide.

*Satisfactory elemental analysis have been obtained for all the compounds reported.

Experimental*

3-Mercaptoanisic acid: To a warm acetic acid solution (100 ml) of 3-chlorosulphonylanisic acid (0.02 mole), prepared in 68% yield by the chlorosulphonation of anisic acid[4], was gradually added with swirling $SnCl_2$ (0.05 mole) dissolved in conc. HCl (12 ml). The mixture was refluxed for an hour, cooled and poured into cold water (600 ml) containing conc. HCl (25ml). The precipitate obtained was filtered, washed with water and crystallised from acetone to give pale yellow crystals. m.p. 236° (lit. 220°[3] and 317°[1]). Yield 81.5%. (Found : C, 52.03 ; H, 4.20 ; S, 17.3 Calcd. for $C_8H_8O_3S$; C, 52.18 ; H, 4.35 ; S, 17.39%).

6,6'-Dimethoxy-3, 3'-dicarboxydiphenyl disulphide: The mercaptan on oxidation with Na_2CO_3 and I_2 solution gave the disulphide, $C_{16}H_{14}O_6S_2$, m.p. 339° in 67.5% yield.

Ethyl-3-carboxy-6-methoxyphenyl sulphide: Sodium (2 g) was gradually added to refluxing dry ethanol (40 ml) followed successively by 3-mercaptoanisic acid (0.01 mole) and ethyl bromide (5 ml). The reaction mixture was refluxed for 2 hr, water (10 ml) added and the excess ethyl bromide and ethanol distilled off. The aqueous solution on acidification gave the desired compound, $C_{10}H_{12}O_3S$, crystallised from ethanol (30%) in white flakes m.p. 139° in 73% yield.

3-Cabroxy-6-methoxyphenylthioglycollic acid: 3-Mercaptoanisic acid (0.01 mole) was condensed with chloroacetic acid (0.01 mole) using alc. KOH[5]. The product $C_{10}H_{10}O_5S$, m.p. 214° (50% ethanol) was obtained in 68% yield.

3-Carboxy-6-methoxy-4'-nitrodiphenyl sulphide: 3-Mercaptoanisic acid (0.01 mole) was condensed[6] with 4-chloronitrobenzene (0.01 mole) using alc. KOH. Yield 58.7%, m.p. 210° (ethanol). It analysed for $C_{14}H_{11}O_5NS$.

4'-Amino-3-carboxy-6-methoxydiphenyl sulphide: Best yield of the amine was obtained when the above nitro derivative was reduced in ethanol with Sn and HCl. After the reduction, the *p*H was raised to 6-7 with NaOH and the precipitated amine was extracted with ethanol. It was dissolved in 20% $NaHCO_3$, filtered and acidified with AcOH. It was crystallised from ethanol to give pale brown crystals, m.p. 250°, in 56% yield. (Found : C, 60.91 ; H, 5.0 ; N, 5.09 ; S, 11.91. Calcd. for $C_{14}H_{13}O_3NS$: C, 61.09 ; H, 4.73 ; N, 5.1 ; S, 11.63%).

The amine was characterised through its acetyl ($C_{16}H_{15}O_4NS$, m.p. 287°), tosyl ($C_{21}H_{19}O_5NS_2$, m. p. 226°), brosyl ($C_{20}H_{16}O_5BrNS_2$, m. p. 232°), N-substituted phthalimide ($C_{22}H_{15}O_5NS$, m.p. 241°), N-substituted-3- nitrophthalimide ($C_{22}H_{14}O_7N_2S$, m.p. 274°) and N-substituted succinimide ($C_{18}H_{15}$-O_5NS, m.p. 216°) derivatives.

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Spectrophotometric Determination of Manganese Employing N-Hydroxy-N-phenyl-N′-benzylbenzamidine Hydrochloride (HPBBAH)

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FASCINATED by the analytical potentialities of N-hydroxy-N,N′-diarylbenzamidines[1-5], it was thought worthwhile to synthesise and investigate the complexing properties of a hydroxyamidine analogue in which a methylene group is introduced in between azomethine nitrogen atom and the N′-aryl ring. Thus, in the course of the study, it is found that N-hydroxy-N-phenyl-N′-benzylbenzamidine hydrochloride, abbreviated as HPBBAH, reacts with many transition metal ions in a manner analogous to other hydroxyamidines. However, a distinct change in its behaviour with manganese(II) has been noted. Whereas the hydroxyamidines reported earlier[6,7], develop a yellow-green colour with manganese(II) in ammoniacal medium[8], HPBBAH gives an instantaneous and sensitive blue colour in ethanol. Based on this colour reaction, a simple rapid and sensitive spectrophotometric method has been developed for the determination of microgram quantities of manganese.

Experimental

Preparation and the properties of the reagent : HPBBAH was prepared by coupling equimolar ethereal solutions of N-benzylbenzimidoyl chloride and N-phenylhydroxylamine at 0-5° following the general method for the synthesis of hydroxyamidines[6]. The resulting white solid after washing with ether was recrystallised from absolute alcohol containing a few drops of HCl . White shining crystals of the compound melted at 195° ($C_{20}H_{19}N_2OCl$. requires : C,70.93 ; H, 5.61 ; N, 8.27%, found : C, 70.85 ; H, 5.76 ; N, 8.20%)

IR Spectra (nujol-hexachlorobutadiene) : νmax, 2450 ($=\overset{+}{N}$-H) ; 1620 ($-C=\overset{+}{N}H$) ; 935 (N-O) cm^{-1}.

UVSpectra : λ_{max}^{EtOH} , 213 nm (ϵ, 22500) ; 300 nm (ϵ, 7050).

A 2% solution of the reagent in ethanol was employed for the development of the colour.

A stock solution of manganese(II) was prepared by dissolving $MnCl_2.2H_2O$ in double distilled water containing few drops of HCl. The solution was standardised complexometrically[9,10]. Solutions of diverse ions were prepared from analytical grade chemicals.

Infrared and ultraviolet spectra were recorded on Perkin-Elmer 221 and Carl-Zeiss 'Specord' (UV/VIS) spectrophotometers respectively. Absorbance measurements were made with an ECIL GS-865 spectrophotometer equipped with 1 cm matched cuvettes. The *p*H of the solutions were measured with a Systronic *p*H meter type 322.

Recommended procedure for the determination of manganese : To a suitable aliquot (1-2 ml) of the solution containing 10-100 μg of the metal, taken in a 10 ml volumetric flask, add 2 ml of the reagent solution. Adjust the *p*H to 8.4-9.8 with dilute ammonia and allow to stand for 2 min with occasional shaking. Dilute to volume with enough water and ethanol so as to give a final 70% concentration of the latter. Measure the absorbance at 590 nm against alcohol as blank.

Results and Disscussion

The instantaneously developed manganese-HPBBAH complex shows an absorption maxima at 590 nm. The reagent has practically no absorbance at 450 nm and above and hence for all photometric measurements alcohol was used as blank. The colour is stable atleast for 2 hr in the temperature rang 20-40°. The absorption of the complex remains constant and maximum in the *p*H range from 8.4 to 9.8. Therefore, a *p*H value of 9.1 $\pm$0.1 was arbitrarily chosen for the spectrophotometric studies. To achieve maximum colour development, a 1 to 80 molar ratio of the metal to reagent is necessary. In practice, for every 100 μg of the metal 40 mg of the reagent was employed. A 1 : 400 manganese to ligand ratio has been studied to have no adverse effect on the determination. The order of the addition of the reagents is critical.

The system adheres to Beer' law upto 10 μg/ml of manganese cocentration. Ringbom's plot[11] suggests an effective metal concentration range of 2.0-9.0 ppm. The molar absorptivity of the complex is 5.33×10^3 litre $mole^{-1}$ cm^{-1} at 590 nm (on the basis of the manganese content). The sensitivity of the colour reaction according to Sandell's definition[12] (log $I_0/I=0.001$) is 0.0103 $\mu g/cm^2$. Ten independent determinations on solutions each containing 50 μg of Mn(II)/10 ml gave a mean absorbance value of 0.485 and a standard deviation of $\pm$0.003 or a relative standard deviation of $\pm$0.61%. The method is, thus, fairly precise and reproducible.

Interference :

In the determination of 5 ppm of manganese at pH 9.1±0.1 the following ions do not interfere to the extents (μg/ml) given in the parentheses: CH_3COO^-, Cl^-, Br^-, I^- SO_4^{2-}, NO_3^-, or $B_4O_7^{2-}$ (500); PO_4^{3-} (100); Na^+, K^+, Li^+, Rb^+ or Cs^+ (500); Ba^{2+} or Sr^{2+} (250); Ag^+ (50); Cd^{2+}(20); MoO_4^{2-} or WO_4^{2-}(20). However, Cu^{2+}, Pd^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, VO_3^-, EDTA and fluoride seriously interfere at all concentrations. The use of common masking agents to eliminate their interferences was not fruitful.

Acknowledgement

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Simultaneous Spectrophotometric Determination of Vanadium and Uranium with 4-Methyl Daphnetin

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VANADIUM and uranium metals are frequently mined together. Although reliable analytical procedures for their determination are known, very little work has appeared on the simultaneous spectrophotometric analysis of these metals.

4-methyl daphnetin forms an orange-yellow complex with uranium (λ_{max} 450 nm) and a bluish-green complex with vanadium (λ_{max} 600 nm) in the pH range 5 and 7. The present work reports a simple and quick simultaneous spectrophotometric method of analysis of vanadium and uranium with 4-methyl daphnetin.

From the spectrophotometric properties of the complexes.

Complex	λ_{max} nm	ε_{450}	ε_{600}	Sandell sensitivity μg/cm²
V(v)-4-methyl daphnetin	600	6375	900	0·006
U(vi)-4-methyl daphnetin	450	2700	0	0·030

The relationships (1) and (2)

$$A_{450}=\varepsilon^{V}_{450}[V]+\varepsilon^{U}_{450}[U] \quad (1)$$

$$A_{600}=\varepsilon^{V}_{600}[V]+\varepsilon^{U}_{600}[U] \quad (2)$$

were used to develop the following equations :

$$[V]\times 10^{4} = 1.266\ A_{600}$$
$$[U]\times 10^{4} = 3.7\ A_{450} - 3.4\ A_{600}$$

Several synthetic mixtures were prepared and analysed satisfactorily.

Procedure

To an aliquot containing 0.8 to 1.6 μg of V (v) and 10-25 μg of UO_2^{2+} is added 4 ml of 0.1M alcoholic solution of 4-methyl daphnetin. The pH of the solution is adjusted between 5 and 7 and the resulting solution diluted to 25 ml. The absorbance of the solutions are measured at 450 and 600 nm against the corresponding reagent blank. The amounts of metals are computed from the appropriate simultaneous equations. A large number of anions do not interfere in the estimation, however Mo, Fe, Ti, W interfere and should be eliminated.

Structures of the Reaction Products from Reaction of Resorcinol with N-Benzoyl Phthalimide

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AN organic dye has been synthesised by the condensation of Resorcinol with N-Benzoyl phthalimide which is a known compound. It behaves like florescene, a dye.

Experimental

Three gms. of phthalimide was benzoylated by the usual procedure[1]. The crude N-benzoyl phthalimide was crystallised from ethanol, m.p. 115°, yield 0.8 gm.

Found : C=71.8, H=3.8, N=5.3% Molecular weight by Rast=248. Calculated for $C_{15}H_9O_3N$, C=72.1, H=3.57, N=5.5% Moleculer weight 251.

Condensation of Resorcinol with N-benzoyl phthalimide[2] :

Three gms. of the benzoyl derivative was condensed with 6 gms. of resorcinol in presence of conc. H_2SO_4 on a sand bath till it attained a reddish brown colour. It was diluted with water neutralised with 200 gms. of $BaCO_3$ and filtered. The filtrate was concentrated on a water bath. The residue was dried in vacuum dessicator.

Purification :

The mass was completely dried in a drying pistol and the dried mass was treated with absolute alcohol. Some portion of the dried mass was dissolved in alcohol. The alcohol was distilled and the residue was dried over anhydrous $CaCl_2$ in a vacuum dessicator. This dried mass when subjected to TLC gave two distinct spots showing it to be a mixture of two components.

Separation of two components from its mixture :

The dried mass was treated with acetone when a small amount of the dried mass dissolved leaving behind a residue.

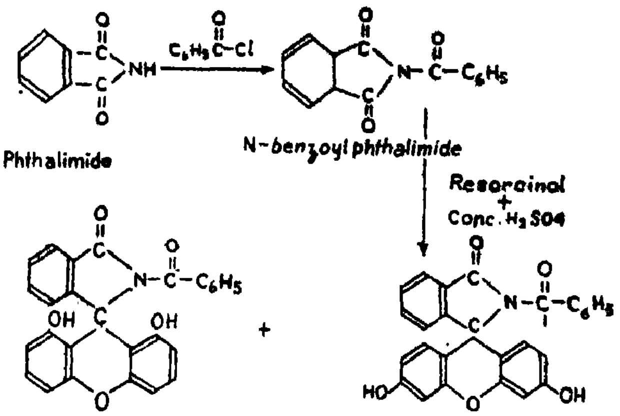
(a) *The acetone soluble component* :

The acetone was distilled and the concentrated syrupy mass was crystallised after cooling in an ice bath into a reddish brown amorphous powder, yield 1.20 gms. It gave a greenish violet fluorescene in dil. NaOH. solution.

(b) *The acetone insoluble component* :

It was dried by evaporating the adhered acetone and then crystallised from absolute alcohol into dark brownish amorphous powder yield 1.6 gms. It also gave a dull green violet fluorescene in dil. NaOH.

From the above experiments, it was concluded that during condensation N-benzoyl phthalimide which has three carbonyl groups i.e. (A, B & C) might react with resorcinol so that the carbonyl group (A) reacts giving different products (1) and (2) as given in Figure.



Both these compounds gave a violet blue coloration with $FeCl_3$ showing the presence of phenolic groups. Being isomeric the compound 1 & 2 gave the micro analysis result which are as follows :

Compound No. 1

Found C=72.3, H=4.2, N=3.4% Mol. wt. by Rast 432 Calculated for $C_{27}H_{17}O_5N$, C=72.1, H=3.9, N=3.2% Mol. wt, 435.

Compound No. 2

Found C=72.18, H=4.16, N=3.4% Mol. wt. by Rast 434 Calculated for $C_{27}H_{17}O_5N$, C=72.1, H=3.9, N=3.2% Mol. wt. 435

Further the confirmation of two different isomers was done on the basis of their IR spectra[3].

IR spectra of compound (1)

700 cm^{-1}, 1075 cm^{-1} Mono substitution in benzene ring, 1085 cm^{-1} 1126 cm^{-1} o-disubstituted benzene ring (strong) 750 cm^{-1} 1, 2, 3 Trisubstituted benzene ring, 1580 cm^{-1} carbonyl groups attached to benzene ring, 1620 cm^{-1} for phenyl group and 1200 cm^{-1}, 1410 cm^{-1}, 3600 cm^{-1}, for phenolic OH group. 1270 cm^{-1} for aromatic ether linkage.

IR spectra of compound (2)

700 cm^{-1}, 1075 cm^{-1} mono substitution,in benzene ring, 1085 cm^{-1}, 1126 cm^{-1} 0-disubstitution, 1170 cm^{-1} 1,2,4 trisubstituted benzene ring, 1580 cm^{-1} carbonyl groups attached to benzene ring; 1620 cm^{-1} for phenyl group and 1200 cm^{-1}, 1410 cm^{-1}, 3600 cm^{-1} for phenolic OH group, 1270 cm^{-1} for aromatic ether linkage.

The main difference between the two spectras were in the peaks at 750 cm^{-1} for 1, 2, 3 trisubstituted and 1170 cm^{-1} for 1, 2, 4 trisubstituted benzene rings in structure (1) and (2) respectively.

On the basis of above difference in the peaks the compound No. 1 gives dull coloured fluorescene

due to the presence of shorter conjugated chain for resonance while the compound No. 2 shows deep coloured fluorescene due to the presence of long conjugated chain for resonance (according to E. R. Watson theory of color).

Acknowledgement

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Phytochemical Studies on *Salvia coccinea* Linn

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In view of the high medicinal importance and utility of *Salvia species*[1] (*Family-Labiate*) in various ailments such as diarrhoea, haemorrhoids, lung diseases, gangrene etc., a systematic chemical investigation of *Salvia coccinea*[2] Linn. on which no phytochemical work seems to have been done so far, has been undertaken in this laboratary. It is a slender herb, 1-2 ft. high ; native of S. America. It also grows between 3500-7000 ft. in the West Himalayas.

The air derid powdered whole plant of *S. coccinea* (1.5 Kg.) was extracted successively with petroleum ether (60°-80°) and benzene.

Petroleum ether concentrate was subjected to chromatography over Brockmann alumina. Elution with petroleum ether-benzene (1 : 1) mixture yielded a compound (0.02 gm.) which on crystallisation from acetone gave a colourless solid m.p. 84°-85°. The I. R. spectrum of the solid discloses its alcoholic nature (ν_{max} . 3300 cm^{-1} associated-OH). The mass spectrum of the compound in addition to molecular ion peak at $^m/_e$ 452, exhibits ion peaks at $^m/_e$ 434 (M-18) and $^m/_e$ 31 (-CH_2OH). The physical properties of the compound were found to be very similar to those reported for n-hentriacontanol[3] which was finally confirmed by the direct comparison (m.m.p., Co.T.L.C. & CO.I.R.) with an authentic sample of n-hentriacontanol.

Elution with benzene afforded a product (0.15 gm.) which on crystallisation from methanol gave shining white flakes, m.p. 134°-136°. It showed bluish-violet colouration with Leibermann-Burchardt test for sterol (ν_{max} . 3560 cm^{-1} for hydroxyl and 1649 cm^{-1} for unsaturation). The mass spectrum of the compound recorded fragment ion peaks at $^m/_e$ 396 (M-18), 273 (M-side chain, $C_{10}H_{21}$) and $^m/_e$ 255 [(M-18)-side chain. i. e., $C_{10}H_{21}$], besides the molecular ion peak at $^m/_e$ 414. It forms an acetate m.p. 128° and a benzoate, m.p. 142°. The identity of the compound as β-sitesterol has eeen established by m.m.p. determination. Co-T.L.C. and CO. I.R. with the authentic specimen of the compound.

Further elution with benzene furnished a very small quantity (0.005 gm.) of another crystalline solid, m.p. 210°-212°, which responds to positive Leibermann-Burchardt test for triterpene. Further characterisation of the compound was not possible due to paucity of the material.

The benzene extract on chromatography over Brockmann alumina in the usual way afforded only β-sitosterol in the benzene chloroform (1 : 1) eluate.

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Chemical Constituents of *Rumex orientalis* Bernh

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RUMEX orientalis Bernh. syn. *Rumex patientia* Linn, a native of Europe, is found in Western Himalayas from Kumaon to Kashmir. Its roots are reported to be used as purgative[1], and are known to contain some anthraquinone derivatives[2]. A survey

of the literature shows that chrysophanic acid and rheochrysidin (physcion) have already been isolated from *R. orientalis*[3]. In the present paper, we report the isolation of nepodin (I), tricosanol (II), β-sitosterol (III) and emodin (IV) from the roots of this plant.

Pet. ether (60°-80°) extract of air-dried powdered roots was subjected to silicagel chromatography. Elution with Pet. ether-benzene (4 : 1) yielded compound (I) which crystallised as pale yellow needles from *n*-hexane m.p. 162°-163°. NMR (100 MHz, $CDCl_3$) δ : 2.52 s, $-CH_3$ protons ; 2.64 s, $-COCH_3$ protons ; 6.84 s, 4-H ; 7.44 d (J=9 Hz), 5-H and a multiplet between 6.8 and 7.0 due to 6-H and 7-H. MS : M^+ 216 and other prominent peaks at m/e 201, 198, 155, 127 and 115. Its identity was finally confirmed as nepodin by mmp, Co-TLC and superposable IR. Diacetate m.p. 186-7°, identical with nepodin diacetate (CO-TLC, IR and mmp).

Further elution of the column led to the isolation of chrysophanic acid (Pet. ether-benzene 4 : 1) and physcion (Pet. ether-benzene 3 : 2). Combined benzene and benzene-chloroform (1 : 3) eluates yielded a residue giving positive L.B. test. This on rechromatography over silicagel column afforded compound (II) m. p. 73°-74° (Pet ether-benzene 3 : 1), which was identified as tricosanol (mmp and Co-TLC) by comparison with an authentic sample. Pet. ether-benzene (1 : 1) eluate yielded compound (III), m.p. 136°, identified as β-sitosterol by CO-TLC, IR and mmp.

Ether extract of the powdered roots was chromatographed over a silina gel column. Benzene-chloroform (1 : 1) eluate furnished compound (IV) m.p. 253-255°. It was identified as emodin by mmp, CO-TLC, superposable IR, NMR and MS which were identical with that reported for emodin[4].

Acknowledgement

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Some 6:8-Dichloro-S-Substituted-2-Mercapto-3-Aryl (or Alkyl)-4-Quinazolones

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In view of the broad spectrum biological activities associated with 4-quinazolones[1-5], it seemed of interest to synthesize 6 : 8-dichloro-s-substituted-2-mercapto-3-aryl (or alkyl)-4-quinazolone derivatives and evaluate them for their activities. The therapeutic effect of 4-quinazolone derivatives has been demonstrated in the case of siamian and avian malarial infections. The anticonvulsant properties of QZ-2(2-methyl-3-*o*-tolyl-4-quinazolone, available commercially as Melsedin) have been reported in mice, rats and dogs[6-9]. A potent anticonvulsant property of BDH 1880 (2-methly-3-*p*-bromophenyl-4-quinazolone hydrochloride) has been reported against matrazole induced convulsions in mice[10].

The above findings have led the authors to synthesize some 6 : 8-dichloro-2-thio-3-aryl (or alkyl)4-quinazolones by condensing aryl or alkyl-isothiocyanates with 3 : 5-dichloro-anthranilic acid in dry ethanol, and alkylating these 4(3H)-quinazolones with alkyl halides in alcoholic alkaline solution. That the alkylation occured at the sulphur rather than the nitrogen atom was proved for a representative member of the series by hydrolysis to the corresponding mercaptan.

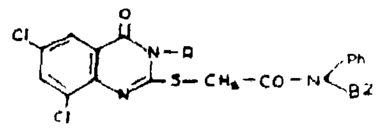
Experimental

6 : 8-Dichloro-2-thio-3-aryl (or alkyl)-4-quinazolones were prepared as described earlier[11].

6 : 8-Dichloro-2-(N, N-benzylphenylcarboxamidomethylthio)-3-phenyl-4-(3-H)quinazolone : 6:8-Dichloro-2-mercapto-3-phenyl-4-(3H) quinazolone (3.2 g) was dissolved in 10% alcoholic sodium hydroxide solution and filtered. In the filtrate, N-benzylchloroacetanilide (2.8 g) dissolved in minimum quantity of ethanol was added and the mixture was stirred vigorously for one hour at room temperature. The crystalline product obtained was filtered, washed 3 or 4 times with water and then with a little ethanol. Finally it was recrystallized from ethanol, m.p. 142°, yield 50%. (Found : N, 7.42 ; S, 5.66. $C_{29}H_{21}Cl_2N_3O_2S$ requires N, 7.69 ; S, 5.86%).

Similarly, other 6 : 8-Dichloro-2-(N,N-disubstitutedcarboxamidomethylthio)-3-aryl (or alkyl)-4-(3H) quinazolones were prepared. They were crystallized from ethanol. Their yields, melting points and analytical results are recorded in Table 1.

TABLE—1 6 : 8-DICHLORO-2-(N, N-BENZYLPHENYLCARBOXAMIDOMETHYLTHIO)-3-ARYL (OR ALKYL)-4 (3H) QUINAZOLONES.



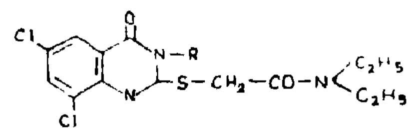
where, R = Aryl or Alkyl
Bz = Benzyl

Sl. No.	Aryl (or Alkyl) group R.	M.P. °C	Molecular formula	Nitrogen, % Found	Calcd.
1.	Phenyl	142	$C_{29}H_{21}Cl_2N_3O_2S$	7.42	7.69
2.	*p*-Tolyl	104	$C_{30}H_{23}Cl_2N_3O_2S$	7.28	7.49
3.	*m*-Chlorophenyl	270	$C_{29}H_{20}Cl_3N_3O_2S$	7.92	7.23
4.	Ethyl	202	$C_{25}H_{21}Cl_2N_3O_2S$	8.18	8.43

Yields of the compounds are found in the range of 50-70%. All the compounds were also analysed for S. The analytical results were within ± 0.3% of the calculated values.

Similarly, various 6: 8-dicholoro-2-(N, N-diethyl carboxamidomethyl thio)-3-aryl (or alkyl)-4(3H)-quinazolones were prepared and their yields, melting points and analytical datas are recorded in Table 2.

TABLE—2 6 : 8-DICHLORO-2-(N, N-DIETHYL CARBOXAMIDOMETHYLTHIO)-3-ARYL (OR ALKYL)-4(3H)-QUINAZOLONES.



Where, R = Aryl or alkyl

Sl. No.	Aryl (or Alkyl) group R.	M.P. °C	Molecular formula	Nitrogen, % Found	Calcd.
1.	*o*-Tolyl	218	$C_{21}H_{21}N_3O_2SCl_2$	9.06	9.33
2.	*m*-Chlorophenyl	268	$C_{20}H_{18}N_3O_2SCl_3$	8.65	8.92
3.	*o*-Methoxyphenyl	192	$C_{21}H_{21}N_3O_3SCl_2$	8.80	9.01
4.	*p*-Ethoxyphenyl	234	$C_{22}H_{23}N_3O_3SCl_2$	8.51	8.75
5.	Ethyl	230	$C_{16}H_{19}N_3O_2SCl_2$	10.50	10.82
6.	Butyl	276	$C_{18}H_{23}N_3O_2SCl_2$	9.80	10.09
7.	Benzyl	200	$C_{21}H_{21}N_3O_2SCl_2$	9.10	9.33

6-8-Dichloro-2-(N,N-diethyl carboxamidomethylthio)-3-butyl-4-(3H)-quinazolones: In a conical flask 3.0 g of 6 : 8-dichloro-2-mercapto-3-butyl-4-(3H)-quinazolone was dissolved in 1.02 g of sodium hydroxide solution in 100 ml water and N, N-diethylchloro-acetamide (1.64 ml) was added drop by drop at room temperature. The flask was shaken vigorously after each addition. When all N, N-diethylchloroacetamide was added, the flask was shaken for another 40 min. The product was separated, filtered, washed with water and finally with a little ethanol. It was recrystallized from ethanol-acetone (1 : 1) mixture, m.p. 276°, yield 60%. Found : N, 9.80 ; S, 7.40. $C_{18}H_{23}Cl_2N_3O_2S$ requires N, 10.09 ; S, 7.69%).

Yields of the compounds are found in the range of 40-60%. All compounds were also analysed or S. The analytical results were within ±0.35 of the calculated values.

Acknowledgement

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Oxidations with Ammonium Hexanitratocerate(IV). Part I : Milligram Determination of Polycyclic Hydrocarbons

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THE small scale determination of hydrocarbon function has always attracted organic analytical chemists because of the slow reactivity of the function and the lack of a general procedure. Quick and direct methods have been given for the small scale determination of cyclic hydrocarbons[1-3]. Recently the spectrophotometric[4-6], gas chromatographic[7] and fluorescence spectrum techniques[8] have been applied for detection and determination of polycyclic hydrocarbons. Marletta[9] has reviewed in detail the recent developments in the determinatoin of aromatic polynuclear hydrocarbons.

Taking advantage of the oxidising capacity of ammonium hexanitratocerate (iv) in nitric acid medium, a quick, precise and accurate (within 0.3-0.85% error) method has been developed for the milligram determination of polycyclic hydrocarbons at room temperature (25°) within five minutes reaction time.

Experimental

Reagent :

0.1 M Ammonium hexanitratocerate (IV) solution was prepared in 0.5 M nitric acid solution. 0.025 M aqueous ferrous ammonium sulphate solution and 1M sulfuric acid solution were prepared from reagent grade chemicals. 0.001 M aqueous ferroin solution was used as indicator.

Sample solution

40-50 mg. of the hydrocarbon was dissolved in glacial acetic acid in a 100 ml measuring flask. All the hydrocarbons were either recrystallised from the proper solvent till a constant melting point is obtained or procured in the pure form.

Procedure :

Aliquots containing 1-5 mg of the sample were taken in a 100 ml. conical flask and 5 ml. of 0.1 M Ce(IV) solution was added to it. The reaction mixture was allowed to stand for five minutes at room temperature (25°). The reaction was quenched by adding 10 ml 1M sulfuric acid and the content shaken for a minute. The unreacted Ce(IV) was titrated against standard Fe(II) using ferroin indicator. A blank was also run under identical conditions using all other reagents except for the sample. The recovery of the sample was calculated with the difference in the readings of Fe(II) for blank and the actual estimation.

$$\text{mg of hydrocarbon} = \frac{\text{ml of 0.025 } M \text{ Fe(ii) Soln} \times \text{Mol wt. of Hydrocarbon}}{\text{Molecularity}}$$

Results

Results obtained with the recommended procedure are given in the table. The effect of concentration of Ce(IV), varying amounts of hydrocarbon sample, reaction time and temperature was also studied for all the hydrocarbons. On the basis of stoichiometry and the identification of final oxidation products, it is established that all the hydrocarbons get oxidised to corresponding quinones.

The presence of phenols, amines, alcohols and aldehydes interfere in the estimation. However the oxidation of benzene is not possible with the recommended procedure.

Table : Determination of polycyclic hydrocarbons with Ce(iv).

Compound	Amount taken (mg)	Amount recovered (mg)	Molecularity	Deviation %
Naphthalene	1.0100	1.0140	6	+0.39
	3.0300	3.0409	–	+0.36
	5.0500	5.0662	–	+0.32
Anthracene	1 0600	1.0680	6	+0.75
	3.1800	3.1978	–	+0.56
	5.3000	5.3196	–	+0.37
Phenanthrene	1.2800	1.2876	6	+0.59
	3.8400	3.8584	–	+0.48
	5.1200	5.1379	–	+0.35
Acenaphthene	1.3400	1.3486	8	+0.64
	2.6800	2.6952	–	+0.57
	4.0200	4.0332	–	+0.33
Diphenyl	1.6200	1.6284	6	+0.51
	3.2400	3.2552	–	+0.47
	4.8600	4.8740	–	+0.29

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Chemical Constituents of *Eupatorium riparium* Regal[1]

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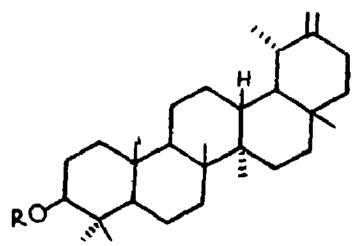
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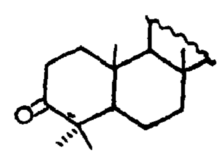
TERPENES, sterols and flavonoids are known to occur in various species of *Eupatorium*; a common genus of the family Asteraceae (Compositae). Recently we reported the occurrence of a new triterpene epoxylupeol[2], lupeol, β-amyrin and a flavone salvigenin[2] from *Eupatorium odoratum*[2,3] and eupacannol, a novel pentacyclic triterpene alcohol with a rearranged ursane skeleton from *Eupatorium cannabinum*[4], both species being collected from Darjeeling. In continuation of our studies on Indian *Eupatorium* species we undertook the chemical investigation of an Indian variety of *Eupatorium riparium* Regel collected from Shillong in the Sub-Himalayan region of north-east India. Earlier workers reported chromenes from the Australian[5] as well as Jamaican[6] variety of the same plant. The present study has revealed the occurrence of taraxasteryl palmitate [urs-20(30)-en-3-β-ol-hexadecanoate: second natural occurrence] as the major product (0.09%) along with taraxasterol (0.01%), stigmasterol (0.02%) and two uncharacterised compounds — an unsaturated liquid hydrocarbon (0.04%) and a microcrystalline solid fatty alcohol (0.02%), m.p. 84-86°.

The light petroleum (b.p. 60-80°) extract of the whole plant of *E. riparium* was chromatographed over silica gel, using solvents of increasing polarity.

Evaporation of the light petroleum eluted fraction furnished an oily residue (two distinct spots in TLC) which could be resolved into a colourless liquid *L* (yield 0.04%) and a crystalline compound I (yield 0.09%) upon repeated chromatographies over silica gel.

Compound I crystallised from ethyl acetate as colourless needles, m.p. 102-03°, $[\alpha]_D$ +70°($CHCl_3$, *c* 0.77); analysed for $C_{46}H_{80}O_2$ (M^+ 664) and showed positive TNM colouration; ν_{max}^{KBr} 1722 cm^{-1} (CO), 1633 (C=C), 863 (=CH_2 out-of-plane bending); PMR (60 MHz, $CDCl_3$) (δ) 2.27 (2H ill-defined *t*, J~6Hz, CH_2CH_2COOR), 4.60 (2H, *m*, C=CH_2), 4.45 (1H, *m*, *H*COCOR, the low field component buried under the C=CH_2 signal). From the above IR and PMR data I was suggested to be an ester. Saponification of I by treatment with 5% KOH solution in tetrahydrofuran-methanol(1:1) at room temperature, followed by usual work up, furnished an acid *A* and a triterpene alcohol II. The acid *A*, crystallised from aqueous ethanol, had m p. 64°. $C_{16}H_{32}O_2$ (M^+256); $[\alpha]_D$ $\pm 0°$; νmax (KBr) 1690 cm^{-1} (CO); weak absorption at 1375 cm^{-1} indicates minimum substitution[7]; PMR (100 MHz, $CDCl_3$); δ 2.29 (2H, *t*, J=7Hz, RCH_2CH_2COOH), a broad singlet at δ 1.26 is assignable to protons of $(CH_2)_n$ indicating the presence of a methylene chain. *A* was identified to be palmitic acid by its mass spectrometry[8] showing M −43 peak (expulsion of C_2, C_3, C_4 and 1H) and other characteristic peaks at m/e (M −43 −14n) and m/e (41+14n) where n= 0,1,2,3...with the decrease of relative intensities as *n* increases, a characteristic of straight chain fatty acid. It was further confirmed by comparison of the GLC curve of its methyl ester (obtained by methylation of *A* with BF_3 in methanol) with that of an authentic sample of methyl palmitate.





I, R=OCO.$(CH_2)_{14}CH_3$
II, R=H
III, R=$COCH_3$

IV

The alcohol II, showing positive Liebermann-Burchardt colouration for triterpenes, crystallised from light petroleum-benzene (1:1) as colourless needles, m.p. 218-19°, $C_{30}H_{50}O$ (M^+426), $[\alpha]_D$ +91° ($CHCl_3$, *c* 0.76); ν_{max} (KBr) 3380 cm^{-1} (OH), 1655 (C=C), 870 (=CH_2 out-of-plane bending); positive TNM colouration: PMR (60 MHz, $CHCl_3$) (δ) 0.76, 0.86, 0.90, 0.97, 1.03 and 1.09 (21H, seven methyls on saturated carbons), 4.60 (2H, *m*, C=CH_2), 3.22 (1H, ill-defined *q*, J_{ax-ax} ~9Hz, J_{ax-eq} ~5Hz, C*H*OH (axial). II formed an acetate III, m.p.243-44°, $C_{32}H_{52}O_2$ (M^+468); $[\alpha]_D$ +107° $CHCl_3$, *c* 0.67); Sarett oxidation of II with CrO_3/Py afforded IV, m.p. 180-81°. $[\alpha]_D$ +127° ($CHCl_3$, *c* 0.69): All these data and the mass fragmentation pattern[9] of II (important ion peaks at *m/e* 411, 408, 357, 344, 315,

207, 189, 136, 135, 109, 107° indicated it to be taraxasterol[10]. Final confirmation was received by direct comparison (m.m.p., co-TLC and superimposable IR spectra) of II, III and IV with the corresponding authentic samples[9].

Characterisation of A and II admitted compound I as taraxasteryl palmitate [urs-20(30)en-3β-ol hexadecanoate]. A thorough literature survey indicated that this is the second report of the natural occurrence of taraxasteryl palmitate which was earleir reported[11] only recently.

Light petroleum-benzene (1 : 1) eluate fractions of the main chromatogram, after evaporation, afforded a gummy residue which upon repeated chromatography over silica gel furnished a fatty alcohol, crystallised from light petroleum as a microcrystaline solid, m.p. 84-86° (yield 0.02%) and a triterpene crystallising from light petroleum-benzene mixture (1 : 1) as colourless needles, m.p. 218-19° (yield 0.01%) characterised as taraxasterol (II) by direct comparison (m.m.p., co-TLC, superimposable IR spectra with an authentic sample).

Evaporation of the benzene eluate fractions of the main chromatogram yielded a gummy residue which upon purification through repeated chromatography afforded a sterol (yield 0.02%) crystallising from light petroleum as colourless needles, m.p. 160-61°. This was found to be identical with stigmasterol by direct comparison (m.m.p., co-TLC, IR).

The liquid *L* (R_f 0.7, silica gel G, light petroleum) with a maximum impurity of 2% as shown in the GLC analysis showed positive TNM colouration. ν_{max} (KBr) 2950 cm^{-1}, 2880 (C-H), 1635 (C=C) indicated it to be an unsaturated hydrocarbon ; comparatively strong absorption band at 1375 cm^{-1} is assignable to a large number of methyl substituents[7]. Further study on compound *L* and the fatty alcohol, m.p. 84-86° are in progress.

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Pd(II) Complexes of N,N′-Substituted Thioureas

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Pd(II) complexes of some N-aryl, N′-2(5-halo pyridyl) thioureas were prepared. IR studies reveal that the complexes formed have 1 : 2 metal to ligand ratio. The metal is linked to the ligands through sulphur of thiocarbonyl group.

Experimental

All reagents used were either of B. D. H. or S. MERK Analar grade. The complexes were prepared by adding ·01*M* soln. of $PdCl_2$ (in butanol) slowly and with constant stirring to a hot solution (0.25*M*) of N-Phenyl, N′-2-(5-Chloro-pyridyl) thiourea, (PCT) : N-Phenyl N′-2-(5-Bromo-pyridyl) thiourea, (PBT) : N-phenyl, N′-2-(5-Iodo-pyridyl) thiourea, (PIT) ; N-O-tolyl-2-5(-Chloro-pyridyl) thiourea, (TCT) ; or N-O-tolyl, N′-2-(5-Bromo-pyridyl) thiourea, (TBT) ; or N-O-tolyl, N′-2-(5-Iodo-pyridyl) thiourea (TIT) in butanol. The complex got precipitated immediately. It was filtered, washed with butanol and then dried in an air at 60-70°.

The composition of complexes was determined by estimation of the elements N, S, Cl and Pd by standard methods. Conductance measurements were made on a conductivity meter, type LBR, WTW, Germany, using a dip type cell. IR in KBr were recorded on a Perkin-Elmer Grating IR Spectrophotometer (Model 237-8).

Results and Discussion

The complexes of PCT, PBT and TCT were reddish in colour whereas that of PIT and PBT were light yellow. They were found soluble in $CHCl_3$ and CCl_4 but were insoluble in ethanol, butanol, water and ether.

The composition of these complexes on the basis of elemental analysis, could be represented by the general formula $PdCl_2L_2$, where L is the appropriate substituted thiourea.

The molar conductance of these complexes in chloroform are found to be quite low (3.2-8.2) showing thereby the non-electrolytic nature of the complexes. This suggests that chlorine atoms are coordinated to the metal ion and are not present in the ionic form.

The bonds occurring at 1600, 1430 and 1060 cm^{-1}, in the IR spectra of the metal complexes were discussed by earlier workers [1-5] to decide the donor atoms of the substituted thiourea. The bands appearing at 1600 cm^{-1} was assigned to (C=C+C=N). Except in two cases this band remains almost constant and thus enables the ruling out of the possibility of metal ligand co-ordination through nitrogen or pyridine ring.

The sulphur of substituted thioureas has been found to be one of the co-ordination sites by various workers in this field [1-6]. Yamaguchi et al [4] were of the opinion that the band assigned to ν(N–C–N+C=S) was more important in the diagnosis of metal-sulphur bond where as Swaminathan et al [5] have given more importance to ν(C=S) band. But the latter band occurs in the region where many other bands of thiourea are also found and hence its detection is associated with quite some difficulty. Banerji et al [2] have observed that these bands show shifts to lower frequencies and/or reduce in intensity in the case of metal complexes of N-N' bis (pyridyl) thiourea. Similar observations (lowering of intensity) have been made in the present case too. Moreover, it is found that the intensity of bands is reduced to such an extent, in some of the cases, that the band either disappears completely or its detection is very difficult. In one case these bands are found to be shifted to even higher frequency with lower intensity. Generally on complexion the ligand stretching frequencies are shifted to lower regions due to a decrease in the band order and consequently the force constant. But in some cases, i.e. in nitrile complexes, the C≡N stretching frequencies [7] and in biuret-metal complexes the N–H stretching frequencies [8] are found to be increased. This suggests the possibility of metal-ligand co-ordination through sulphur of thiocarbonyl group.

Differences in the position and intensity of metal sulphur bands ν(C=S), ν(N–C–N+C=S) in different substituted thiourea complexes may be due to *p*-halo substitution in the pyridyl ring. The electron donating ability of the *p*-halo substituents is in the order I>Br>Cl. The electron from the halo-substituents are donated to the pyridine ring, from where these are delocalized with the thiocarbonyl group. As the electron density in the ground level is increased lesser energy is required for excitation and hence the position of band is shifted to longer wavelengths. The intensity of the transition band, which is related to the probability of the transition is also increased for the same reason. The irregularity observed in present case precludes unambiguous confirmation of hist hypothesis.

On the basis of foregoing discussion it is clearly seen that the substituted thioureas studied form 1 : 2 complexes with $PdCl_2$ in which the thioureas are linked through sulphur to metal and the chlorine atoms remained attached to the metal.

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Syntheses of Copper(II) Complexes with Some new Tridentate Dibasic Schiff Bases

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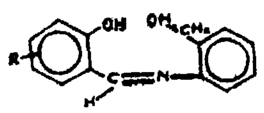
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TRIDENTATE dibasic Schiff bases are novel in the sense that they force the metal (II and III) ions to dimerise of polymerise and as a result metal complexes with unusual magnetic and structural properties are formed[1,2]. There has been considerable interest on the syntheses and magnetic properties of copper (II) complexes of ONO donor tridentate dibasic Schiff bases derived from salicylaldehyde or substituted salicylaldehyde and orthoaminophenol[3]. In this preliminary communication we report the syntheses of serveal new copper (II) complexes with the ligands

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(I) derived from salicylaldehyde, 5-chlorosalicylaldehyde, 5-bromosalicylaldehyde, 3-methoxysalicylaldehyde, 2-hydroxy-1-naphthaldehyde and orthoaminobenzylalcohol. This is the first report on the metal complexes of these new ligands and we intend to make a comprehensive study of coordination behaviour of these ligands with various metal ions.



I. R = H, 5-chloro, 5-bromo, 3-methoxy, 5, 6-benzo.

General method of syntheses of the complexes :

A methanolic solution of the appropriate Schiff base (0.005 mole in 50 ml) was added slowly to a methanolic solution (30 ml) of copper (II) acetate monohydrate (0.005 mole) and the mixture was refluxed for 2 hr while stirring magnetically. The separated precipitates were suction filtered, washed with methanol and dried under vacuum at room temperature. The analytical data are persented in Table 1.

The infrared spectra of the complexes do not exhibit the νOH stretch and this is indicative of the deprotonation of the ligands and dibasic behaviour with oxygen coordination of the ligands. The complexes are insoluble in common solvents and melt or decompose at >250°. This indicates dimeric or polymeric nature of the complexes. The magnetic susceptibilities of the complexes were measured by the Gouy method using $Hg[Co(NCS)_4]$ as the standard. The room temperature magnetic moments of the complexes are in the range 0.98-1.45 B.M. which is less than the spin-only value of 1.73 B.M. required for an $S = \frac{1}{2}$ system. The low magnetic moments are attributed to the antiferromagnetic exchange between the interacting Cu^{2+} ions[4]. The copper(II) complexes of comparable ligands viz. the Schiff bases derived from salicylaldehyde or substituted salicylaldehyde and orthoaminophenol exhibit low magnetic moments and are involved in antiferromagnetic exchange[3].

The complexes exhibit a d-d band at 15400-17100 cm^{-1} (reflectance spectra, Table 1). The origin of a band at around 27000 cm^{-1} in these complexes is due to the symmetry forbidden ligand ⟶ metal charge transfer transition rather than to the binuclear species[5,6]. The infrared bands at 1600-1615 cm^{-1} can be attributed to the coordinated ν(C=N) stretch involving coordination through the nitrogen atom of the azomethine group since the free ν(C=N) stretch is known to appear at around 1640 cm^{-1} in aromatic Schiff bases[7,8].

The cryomagnetic and ESR studies of the complexes are in progress and details will be reported in due course.

Acknowledgement

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TABLE—1 THE ANALYTICAL, INFRARED AND ELECTRONIC SPECTRAL DATA OF COPPER(II) COMPLEXES[a]

Complex		%Cu	%N	μ_{eff} B.M.	ν(C=N) cm^{-1}	ν_{max} cm^{-1}
Cu(sal-*o*-aminobenzylalcohol)	Found:	21.8	4.9	0.98	1610	17100
	Reqd. :	22.01	4.85			
Cu(5-chlorosal-*o*-aminobenzylalcohol)	Found:	19.4	4.1	1.39	1615	15400
	Reqd. :	19.66	4.33			
Cu(5bromosal-*o*-aminobenzylalcohol)	Found :	17.0	3.8	1.45	1615	16400
	Reqd. :	17.28	3.82			
Cu(3methoxysal-*o*-aminobenzylalcohol)	Found :	19.9	4.4	1.40	1600	not measured
	Reqd. :	19.94	4.39			
Cu(hydrox-*o*-aminobenzylalcohol)	Found :	19.1	4.1	1.31	1615	15400
	Reqd. :	18.75	4.14			

[a]Abbreviations : sal = salicylaldehyde, 5-chlorosal = 5-chlorosalicylaldehyde, 5-bromosal = 5-bromosalicylaldehyde, 3-methoxysal = 3-methoxysalicylaldehyde and hydrox = 2-hydroxy-1-naphthaldehyde.

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3 : 5 Dibromosalicyl-azide : a Reagent for Identification of Aminoacids

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THE reactivity of Salicyl azide[1] and 5-Chlorosalicyl azide[2] towards amino acids was found to be encouraging; so a new azide with different combination of bromo group substituents namely 3 : 5 dibromo was synthesised and its reactivity to several amino acids has been investigated. These derivatives were crystalline with sharp melting points and could be separated from each other by thin layer chromatography. In quantitative estimation of amino acid derivatives by thin layer chromatography approximately 80% yield was found.

Lellmann and Grothmann[3] and Robertson[4] prepared 3 : 5 dibromo salicylic acid by different methods and the yield of acid was never more than 35%. Other routes for the preparation of 3 : 5 dibromosalicylic acid are also indicated in the literature (Lassar-cohn and Schultze, and Ullmann and Kopetschni[5]), but the yield of product is not satisfactory. Peratoner[6] prepared methyl 3 : 5 dibromosalicylate with hydrochloric acid. C. N. Haksar and R. D. Wankhade[7] prepared it by esterification of 3 : 5 dibromosalicylic acid using Fischer-Speier method. It was converted into 3 : 5 dibromosalicyl hydrazide by 60% hydrazine hydrate. This hydrazide was readily converted into azide by the action of sodium nitrite. These azides give crystalline derivatives with amino acids with sharp melting points.

Thus 3 : 5 dibromosalicyl azide was found to be a prospective reagent for identification of amino acids.

Experimental

Dibromosalicylate (i) : The preparation was carried out according to method of Cahours[8].

Ice cold solution of bromine (16 g) in glacial acetic acid (20 ml) was added slowly in small protions to an ice-cold solution of methyl salicylate (10 g) in glacial acetic acid (30 ml) with thorough shaking. Bromination was carried out at room temperature for one hour. The reaction mixture was cooled in ice and poured into an excess of ice-cold water, when a bulky white precipitate of methyl 3 : 5 dibromosalicylate was obtained along with a small quantity of methyl 5-bromosalicylate. The precipitate was filtered and dried (yield 16 g).

This crude product (10 g) in glacial acetic acid (30 ml) was again subjected to bromination with bromine (5.2 g) in glacial acetic acid (20 ml) as above. This gave a precipitate of pure methyl 3 : 5 dibromo salicylate. It was filtered at the pump, dried and crystallised from aqueous methanol giving colourless needles, m. p. 148° (Lit 148°, 149°, 156°), yield 11 g.

Analysis : Found Br. 52.30%

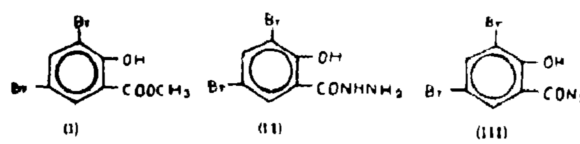
$C_8H_6O_3Br_2$ requires Br 51.61%

3 : 5 Dibromosalicyl hydrazide (ii) : Methyl dibromosalicylate (2 g) was dissolved in methanol (100 ml) and 60% hydrazine hydrate (5 ml) was added. The mixture was refluxed over a water bath for 20 minutes. The solution was diluted with water and cooled. To the cold solution a few mililitres of dilute acetic acid were added, when a voluminous white solid separated. It was filtered and washed with methanol. Yield 1.8 g, caystallised from hot water giving needles, m. p. 217° (decomp.)

Analysis : Found C 27.07%, H 2.23%, N 9.53%. Br 41.47%.

$C_7H_6O_2N_2Br_2$ requires C 27.09%, H 1.93%, N 9.032%, Br 51.61%.

3 : 5 Dibromosalicylazide (iii) : Dibromosalicyl hydrazide (1.5 g) was dissolved in normal nitric acid (15 ml) and water (30 ml), when a clear solution was obtained. This was cooled in ice and 1*N* solution of sodium nitrite (20 ml) was added drop by drop with frequent shaking. The mixture was allowed to stand in ice for one hour, when an olly substance that had separated in the beginning solidified. It was filtered and washed with ice cold water. It was unstable and should therefore be used as quickly as possible.



(i) (ii) (iii)

General method of coupling 3 : 5 dibromosalicyl azide with different amino acids :

The moist dibromosalicyl azide from above was

added in the solution of amino acids in $1N$ caustic soda solution and water. The mixture was shaken and allowed to stand in ice.

The liquid was filtered and the clear filtrate was extracted with ether to remove the unchanged azide. It was then acidified with dilute sulphuric acid. The acid formed during the reaction was immediately extracted with ethyl acetate in which it was soluble at room temperature. The ethyl acetate was then dried over anhydrous sodium sulphate and the excess of solvent was removed by distillation under reduced pressure. On concentration the solid separated.

Following the above procedure a number of derivatives with amino acids were obtained and are given in the table above :

Table

S. No.	Amino acid	Molecular formula	M.P. °C	Analysis% Found	Analysis% Required
1.	Glycine	$C_9H_7O_4NBr_2$	171	C 30.2 H 2.0 N 4.01	C 30.9 H 1.98 N 3.96
2.	Leucine	$C_{10}H_{15}NO_4Br_2$	160	C 39.1 H 3.6 N 3.4	C 39.7 H 3.3 N 3.1
3.	Lysine	$C_{20}H_{19}O_6N_2Br_4$	115	C 34.4 H 2.5 N 3.3	C 34.1 C 2.0 N 3.1
4.	Isoleucine	$C_{13}H_{14}NO_4Br_2$	Above 260	C 38.2 H 3.5 N 3.2	C 38.2 H 3.6 N 3.6
5	Valine	$C_{12}H_{13}NO_4Br_2$	Above 240	C 36.2 H 3.1 N 3.3	C 36.4 H 3.2 N 3.5
6.	Alanine	$C_{10}H_9NO_4Br_2$	Black on 235	C 32.4 H 2,6 N 3.9	C 32.6 H 2.8 N 3.8
7.	Methionine	$C_{13}H_{13}NO_4Br_2$	155	C 33.6 H 3.2 N 4.0	C 33.7 H 3.0 N 3.6
8.	Glutamine	$C_{12}H_{12}O_5N_2Br_2$	185	C 33.5 H 2.9 N 6.0	C 33.9 H 2.8 N 6.6
9.	Glutamic acid	$C_{12}H_{11}O_6NBr_2$	188	C 34.0 H 2.2 N 3.4	C 33.8 H 2.5 N 3.2
10.	Asparagine	$C_{11}H_{10}O_5N_2Br_2$	142	C 32.5 H 2.5 N 3.6	C 32.2 H 2.4 N 3.4
11.	Cysteine	$C_{10}H_9O_4NSBr_2$	140	C 30.2 H 2.4 N 4.0	C 30.0 H 2.2 N 3.8

All the melting points are uncorrected.

Acknowledgement

A generous gift of various amino acids used during this work from (the late) Dr. Ajai Haksar of the Worester Foundation for Experimental Biology, Shrewsburg (U. S. A.) is gratefully acknowledged. Micro-analyses were kindly carried out by the scientists of the C.D.R.I. Lucknow. The award of a U.G.C. research scholarship and a research grant to one of us (S.S.) is also gratefully acknowledged.

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A new Method for Determination of Solubility Product of Silver Bromide

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WHEN two solutions of uni-univalent electrolytes having a common ion and same concentration have a junction then both Henderson's and Planck's equations for liquid junction potential (E_L) give

the same value ; $E_L = \frac{RT}{F} l_n \frac{\Lambda_1}{\Lambda_2}$ where Λ_1 and Λ_2 are equivalent conductance of the two electrolytes. Specific conductance κ_1 and κ_2 can take the place of Λ_1 and Λ_2 in this equation. This equation is also known as Lewis and Sargent equation. A good account of liquid junction potential is given in MacInnes "Principles of Electrochemistry, 1939 edition, Chapter 13." In an electrochemical cell of the type,

$$\mathrm{Ag}\left|\mathrm{AgBr}\ \begin{matrix}\mathrm{NaNO_3(c_1)}\\ \mathrm{KNO_3(c_2)}\\ \mathrm{Satd.\ with}\\ \mathrm{AgBr}\end{matrix}\right|\begin{matrix}\mathrm{NaNO_3(c_1)}\\ \mathrm{KNO_3(c_2)}\end{matrix}\left|\begin{matrix}\mathrm{AgNO_3}\quad \mathrm{AgBr}\\ (c=c_1+c_2)\end{matrix}\right|\mathrm{Ag},$$

the liquid junction potential can be eliminated (on the basis of the above equation), if κ_1 is made equal to κ_2 by taking (a) a mixture of two uni-univelent electrolytes of concentrations c_1 and c_2 having a common ion on one side of the junction and (b) one uni-univalent electrolyte of concentration c on the other side having the common ion. Now κ_1 can be made equal to κ_2 and the concentration of the common ion kept the same on two sides of the junction by making $c=c_1+c_2$ and $\Lambda c=\Lambda_1c_1+\Lambda_2c_2$. c, c_1 and c_2 denote the concentrations (gm.mole/litre) of silver nitrate, sodium nitrate and potassium nitrate respectively. Further Λ, Λ_1 and Λ_2 denote the equivalent conductances of silver nitrate, sodium nitrate and potassium nitrate at $\mu=c$.

There is no general equation connecting equivalent conductance and temperature. Equivalent conductance at all temperatures are not recorded in literature. In the small region of temperature in which the work was done, equivalent conductance of the three salts varies linearly with temperature. So there was no difficulty in finding the required values of Λ, Λ_1 and Λ_2 at the concerned temperatures. No value of μ was selected for which Λ, Λ_1, Λ_2 and were not known at a number of temperatures.

The above cell has been used in determining the solubility product of silver bromide at 45°.

Experimental

All solutions were prepared in double-distilled water from G.R. quality salts at the experimental tempetature. Silver-silver bromide electrode was prepared on a platinum spiral depositing silver electrolytically[1] and bromidising in 0.1*N* KBr solution[2]. The solution in L.H.S. half cell was saturated with thoroughly washed silver bromide to prolong the life of the electrode. The electrode vessels, bridge and setting up of the cells were similar to that described earlier[3]. Temperature was 45±0.05°. Tinsley Vernier Potentiometer was used. Duplicate cells invariably used generally agreed within 0 15 mv., difference going up to 0.2mv. in a few cases. The experimental results are given in the following table.

TABLE—1

c_1 $NaNO_3$	c_2 KNO_3	E in abs. volt	$E-\frac{RT}{F}\ln c+\frac{2.3026RT}{F}A\sqrt{\mu}$
0.00377	0.00123	0.21180	0.35941
0.00790	0.00210	0.22945	0.35904
0.01500	0.00500	0.24765	0.35963
0.04166	0.00834	0.27035	0.35995
0.05923	0.01077	0.27880	0.36055
0.08080	0.01920	0.28715	0.36084

Discussion

Charges on the ions may be left out. Let a_{Ag} and f indicate the activity and activity coefficient respectively of A_g^+ in silver nitrate solution and let a^*A_g and a^*B_r indicate the activity of A_g^+ and Br^- in the mixture of sodium nitrate and potassium nitrate. We may assume that up to $\mu=0.1$, $a^*A_g = a^*B_r$ and $\log f_1 = -A\sqrt{\mu}+\beta_1\mu$.

$$\text{The e.m.f. of the cell } E=\frac{RT}{F}\ln\frac{aA_g}{a^*A_g}=\frac{RT}{F}\ln\frac{cf}{a^*A_g}=\frac{RT}{F}\ln\frac{cf}{\sqrt{k_{sp}}}$$

$$\text{or, } E-\frac{RT}{F}\ln c+\frac{2.3026RT}{F}A\sqrt{\mu}=\frac{2.3026RT}{F}.\beta\mu-\frac{2.3026RT}{2F}\log k_{sp}$$

Plot (Fig 1) of L.H.S. (denoted by p) of the above equation against μ is a straight line from which the value of k_{sp} comes out to be 4.101×10^{-12}. When converted to molality scale, it becomes 4.182×10^{-12} against Owen and Brinkley's[4] value of 4.055×10^{-12}, Gledhill and Malan's[5] value of 4.56×10^{-12} and our own value[6] by Owen's method[7] of 3.910×10^{-12}, all on molality scale. Hence the present method is useful.

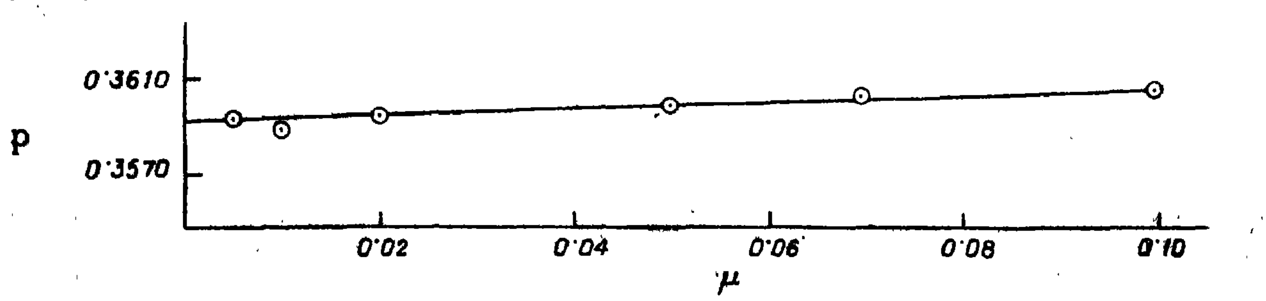


Fig 1

Acknowledgement

We are thankful to the U.G.C. and the Patna University for grants to one of us (A.C.J.) and to the authorities of the Patna University for the library and laboratory facilities.

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Gravimetric Determination of Selenium with Phenylhydrazine

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LITERATURE provides a number of reagent[1-5] for the gravimetric determination of selenium. In most of the procedures recommended, selenium is precipitated as its red variety and must be dried cautiously for 4-6 hr before final weighing. Hydroxylamine method is more suitable for selenium but is still not attractive because of the long time needed for digestion. Hovorka[6] employed hydrazine hydrate in perchloric and hydrochloric acids and reports that the determination of selenium in percholoric acid was unsatisfactory. However, Ooba and Uneo[7] studied this reaction in perchloric acid for determining selenium in chalcogenide materials, prescribed a minimum of 4 hr digestion at boiling water bath temperature. This paper describes an accurate and relatively rapid gravimetric method for selenium.

Phenylhydrazine has been used very largely as a reagent for the characterisation of carbohydrates. The use of this reagent for the analytical determination of metals has been very limited. It has been applied for the determination of micro amounts of selenium colorimetrically[8]. Using this the reduction of selenious acid into elementary selenium is accomplished in both tartaric and hydrochloric acid solutions in about 30 min.

Unlike the existing methods the procedure now proposed is rapid and can be completed in about 2 hr.

Experimental

All the chemicals used were of analytical purity.

Selenium Solution : A standard solution was prepared by dissolving 1.6329 g of selenious acid (BDH AnalaR 2 grade) in one litre of double distilled water. The amount of selenium was determined using hydroxylamine hydrochloride[9].

Reagent Solution : 10 ml of phenylhydrazine was dissolved in 100 ml of rectified spirit.

Recommended Procedure : An aliquot of selenium solution (containing 9.90-99.00 mg of C) was transferred to a 400 ml beaker. To this, tartaric acid (20 g) and appropriate amount of reagent solution (1 ml=20 mg Se) were added. The solution was brought to a final volume of 200 ml with distilled water. The beaker was placed on a boiling water bath and heated for 30 min till the black elemental selenium separated. It was then filtered through a G-4 sintered glass crucible, washed free from excess phenylhydrazine with alcohol and dried at 120° to constant weight. The results are listed in Table 1.

TABLE—1a. DETERMINATION OF SELENIUM
Tartaric Acid 20 g ; Reagent solution, 5 ml.

Amount of Selenium taken mg	Amount of Selenium found mg	Recovery %
99.00	98.90	99.9
49 50	49.40	99.8
49.50	49.45	99.9
24.75	24.70	99.8
9.90	9.88	99.8

TABLE—1b. DETERMINATION OF SELENIUM IN HYDROCHLORIC ACID (2.0 N)

Amount of Selenium taken mg	Amount of Selenium found mg	Recovery %
10.54	10.50	99.8
21.08	21.14	100.2
31.62	31.58	99.9
42.16	42.16	100.0
52.70	52.64	99.9
63.24	63.18	99.9
84.32	84.12	99.8
115.94	115.94	100.0
126 48	126.28	99.8
147.56	147.68	100.1

Results and Discussion

In order to optimise reaction conditions the influence of tartaric acid, reagent concentration and time required for complete precipitation have been investigated.

Effect of Tartaric Acid and Reagent: Both tartaric acid and reagent concentration influence the rapid recovery of selenium (Table 2). Lower

TABLE-2 EFFECT OF TARTARIC ACID AND REAGENT CONCENTRATION ON SELENIUM DETERMINATION.

Se taken	Tartaric acid added.	Phenyl-hydrazine added	Digestion time	Se found	Recovery
mg	g	ml	hr	mg	%
49.50	2.0	0.15	3.0	49.30	99.6
49.50	2.0	0.50	3.0	49.40	99.8
24.75	2.0	1.00	3 0	24.75	99.8
24.75	2.0	2.00	3.0	24.68	99.8
9.90	2.0	5.00	3.0	9.89	99.9
49.50	5.00	0.15	3.00	49.40	99 8
99.00	10.00	0.15	3.00	98.90	99.9
24.75	20.00	0.15	3.00	24.70	99.9
24.75	30.00	0.15	3.00	24.70	99.9
49 50	5.00	0.15	0.5	35.05	70.8
24.75	10.00	0.30	0.5	22.10	89.3
24.75	20 00	0.50	0.5	24 70	99.9
9.90	30.00	0.50	0.5	9.86	99.6

acid concentrations prolonged the reaction time too long for practical purposes. Higher concentrations of tartaric acid were chosen in preference to lower acidities because the reduction of selenium occurred more readily at higher acidities and hydrolysable metals were easily kept in solution. The optimum conditions to achieve the rapid recoveries of the metal are 5 to 15% tartaric acid and 0.5 to 1 ml reagent in a final volume of 200 ml. To ensure rapid recoveries of the metal an excess of reagent (0.5-1 ml) is recommended. A large excess of the reagent upto 5 ml however has no adverse effect.

Time: The minimum digestion time required for the quantitative precipitation to be established by varying the amounts of tartaric acid and phenylhydrazine (Table 2). The selenium completely separated after a brief digestion period of 30 min with 10% tartaric acid and 5 ml reagent solution saving time with no sacrifice of accuracy (Table 1). At lower concentrations of both, the reaction needed 3 hr for completion and the precipitate must be allowed to stand preferably overnight.

Diverse Ions: The method permits the determination of selenium in the presence of appreciable amounts of iron, cobalt, cadmium, manganese, nickel, chloride, sulphate and nitrate. Copper, tellurium, chromium and thorium, however, seriously interfere.

Use of Hydrochloric Acid: The reduction to elemental selenium is also accomplished in hydrochloric acid media at boiling water bath temperature. The reaction is complete in 1.0-6.0 *N* hydrochloric acid, (approximately 10 to 60% by volume). 40 ml of the acid in the total volume of 200 ml was used. The effect of acidity and the time required for complete precipitation are shown in Table 1. The experiments were made by taking varying amounts of selenium as selenious acid adding from 20-60 ml of hydrochloric acid and 5 ml of the reagent. Selenium was determined by the same procedure. In every case the recovery of selenium was quantitative. The precipitation of selenium as its black variety is accomplished in about 30 min. Hydrochloric acid is thus a convenient alternative to tartaric acid.

Acknowledgement

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Kinetics of Oxidation of Oxalic Acid by Ceric Sulphate in Acidic Medium

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CERIC sulphate is one of the strongest oxidising agents with an oxidation potential of 1.43±0.05 Volts in 1-8*N* sulphuric acid[1]. The common valencies of cerium in ceric salts are 3 and 4, in which the probable unhybridised electronic configuration[2] are $5s^25p^64d^{10}4f^1$ and $5s^25p^64d^{10}$ respectively. The kinetic behaviour of the oxidation

of organic substrates by ceric ion present certain interested features. The reference may be given by the studies of a-hydroxy acids done by Dayal and Bakore[3]. The literature shows that only a preliminary work has been done on the oxidation of oxalic acid[4-5] by Ce(IV). We have carried out a detailed kinetic study of oxidation of oxalic acid by ceric sulphate to obtain a deep insight into the reactive species of ceric sulphate.

Experimental

The chemicals used were either "AnalaR or E. Marck's" guaranteed reagent quality. Ce(IV) sulphate solution was prepared by dissolving ceric sulphate in sulphuric acid. The reactive substances were brought to the thermostat temperature maintained to $\pm 0.1°$ and then quickly mixed. Aliquots were withdrawn at known intervals of time and the reaction was quenched by adding ice-cold distilled water and the unconsumed Ce(IV) was estimated with the standard solution of ferrous ammonium sulphate using ferroin as an indicator. The observed pseudo first order rate constant k was calculated from the graph.

Effect of oxalic acid :

To study the effect of oxalic acid concentration, the reaction was carried out at five different initial concentration of oxalic acid and the same inital concentration of sulphuric acid and ceric sulphate. The kinetic data for these studies are summarised in Table-1.

TABLE—1

$10^3 \times$ [Ce(IV)] = 0.40 *M* ; $[H_2SO_4]$ = 2.50 *M* ;
Temp. = 25°

$10^2 \times$ [Oxalic acid] *M*	0.10	0.20	0.30	0.40	0.50
$10^3 \times$ k(min.$^{-1}$)	6.48	8.18	10.18	11.64	14.50

The reaction is found to be pseudo first order w.r.t. oxalic acid which is confirmed by ploting 1/k *Vs.* 1/[oxalic acid]. The plot is a straight line which cuts 1/k axis at a certain distance (Fig. 1).

Effect of Sulphuric Acid :

The effect of sulphuric acid concentration on the reaction has been studied at five different concentration of sulphuric acid as shown in Table-2.

TABLE—2

$10^3 \times$ [Ce(IV)] = 0.40 *M* ; $10^2 \times$ [Oxalic acid] = 0.30 *M* ;
Temp. = 25°

$[H_2SO_4]$M	1.50	2.00	2.50	3.00	4.50
$10^3 \times$ k(min^{-1})	13.56	11.39	10.18	9.41	8.18

The plot of k *vs.* $1/[H_2SO_4]^2$ is a straight line (Fig. 2) which indicates that the rate of reaction is inversely proportional to the square of the concentration of sulphuric acid.

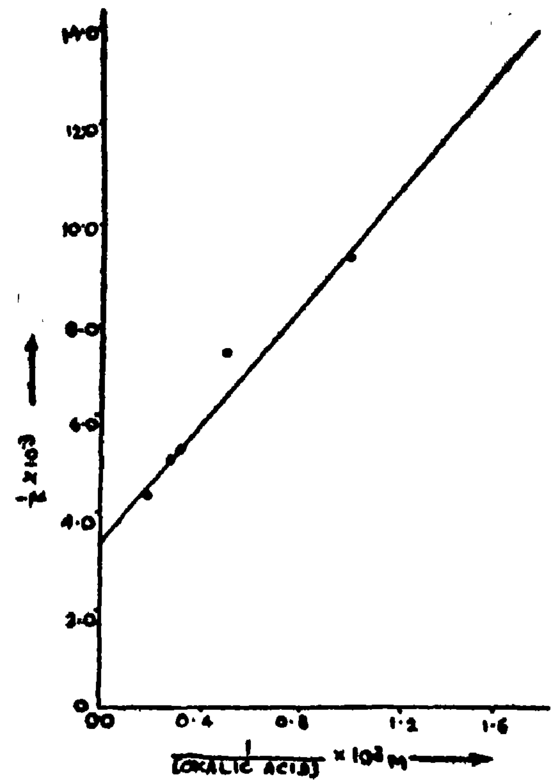


Fig. 1

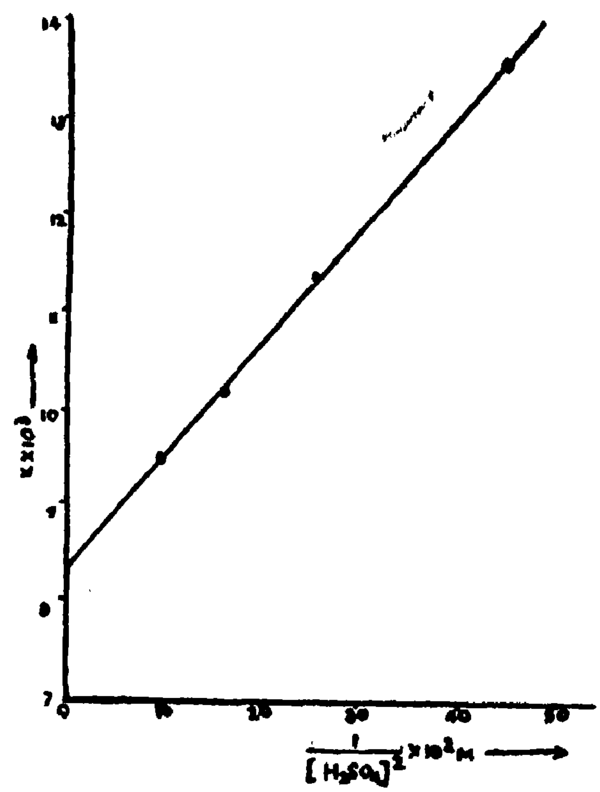


Fig. 2

***Effect of Temperature* :**

The reaction has been studied at different temperatures varying from 288°A to 303°A. The Arrhenius parameters have been calculated and are recorded in Table-3.

TABLE—3

$10^{2}\times[Ce(IV)] = 0.4\ M$; $10^{2}\times$ [Oxalic acid] $= 0.30\ M$; $[H_2SO_4] = 2.5\ M$

Temp. in °A	K × 10^{8} min^{-1}	Energy of activation(E) in Kcals $mole^{-1}$	Frequency factor (A) litre $mole^{-1}$ sec^{-1} A × 10^{-4}	Energy of activation ($\Delta S^{\neq}$) e.u.	Free energy ($\Delta G^{\neq}$) Kcals $mole^{-1}$
288	5.12	-	30.68	- 35.48	22.21
293	8.43	12.24	30.00	- 35.29	22.32
298	10.18	12.58	30.45	- 35.58	22.58
303	15.76	-	30.70	- 35.31	22.68
	Mean	12.58	30.65	- 35.41	22.44

Discussion

The plot of 1/k *vs.* 1/[oxalic acid] is a straight line which cuts 1/k axis at a certain distance. This suggests the formation of activated complex between Ce (IV) and oxalic acid. The activated complex docomposes into organic free radical and Ce(III) through chain mechanism as shown below :

$$\begin{matrix}COOH\\|\\COOH\end{matrix} + Ce(IV) \overset{K_1}{\rightleftharpoons} \left[\begin{matrix}COOH\\|\\COOH\end{matrix}\!\!>\!Ce(IV)\right] \quad ...(1)$$

$$\left[\begin{matrix}COOH\\|\\COOH\end{matrix}\!\!>\!Ce(IV)\right] \xrightarrow{slow} \begin{matrix}CO\dot{O}\\|\\COOH\end{matrix} + H^+ + Ce(III) \quad ...(2)$$

$$\begin{matrix}CO\dot{O}\\|\\COOH\end{matrix} \longrightarrow \begin{matrix}O\\\|\\C-\dot{O}\\|\\C-O^-\\\|\\O\end{matrix} + H^+ \quad ...(3)$$

$$\begin{matrix}O\\\|\\C-\dot{O}\\|\\C-O^-\\\|\\O\end{matrix} \longrightarrow C=O + \begin{matrix}O\\\|\\\dot{C}-O^-\\\|\\O\end{matrix} \quad ...(4)$$

$$\begin{matrix}\dot{C}-O^-\\\|\\O\end{matrix} + Ce(IV) \longrightarrow \begin{matrix}C-O^-\\\|\\O\end{matrix} + Ce(III) \quad ...(5)$$

$$\begin{matrix}C-O^-\\\|\\O\end{matrix} \longrightarrow CO_2 \quad ...(6)$$

The overall oxidation reaction may be written as :

$$\begin{matrix}COOH\\|\\COOH\end{matrix} + 2\,Ce(IV) \longrightarrow 2Ce(III) + 2H^+ + CO_2$$

The above stoichiometric equation is in confirmity with the mole ratio 1 : 2 between oxalic acid and Ce(IV) as determined experimentally. The rate of consumption of Ce(IV) is given by reaction (i) as :

$$-\frac{d[Ce(IV)]}{dt} = K_1[Ce(IV)]\,[\text{Oxalic acid}] \qquad ...(i)$$

According to Hardwick and Robertson[6], the reactive specie ceric sulphate in presence of sulphuric acid gives the complexes as shown below :

$$Ce(SO_4)_2 + HSO_4^- \overset{K_2}{\rightleftharpoons} HCe(SO_4)_3^- \qquad ..(7)$$

$$HCe(SO_4)_3^- + HSO_4^- \overset{K_3}{\rightleftharpoons} H_2Ce(SO_4)_4^{-2} \qquad ...(8)$$

Where K_2 and K_3 are the equilibrium quotients ;

$$K_2 = \frac{[HCe(SO_4)_3^-]}{[HSO_4^-][Ce(SO_4)_2]} \qquad ...(ii)$$

$$K_3 = \frac{[H_2Ce(SO_4)_4^{-2}]}{[HCe(SO_4)_3^-][HSO_4^-]} \qquad ...(iii)$$

from equation (ii) and (iii)

$$[Ce(SO_4)_2] = \frac{[H_2Ce(SO_4)_4^-]}{K_2K_3[HSO_4^-]^2}$$

Substituting the value of $Ce(SO_4)_2$ in eqation (i)

$$-\frac{d[Ce(IV)]}{dt} = \frac{K_1[H_2Ce(SO_4)_4^{-2}]\,[\text{Oxalic acid}]}{K_2K_3[HSO_4^-]^2} \quad ...(iv)$$

As the equilibria of the reaction (7) and (8) are rapid, the $H_2Ce(SO_4)_4^{-2}$ will be proportional to Ce(IV) and on assuming the centpercent dissociation of sulphuric acid into H^+ and HSO_4^- ion, the eqation (iv) is reduced to the form :

$$-\frac{d[Ce(IV)]}{dt} = \frac{K'[Ce(IV)]\,[\text{Oxalic acid}]}{K_2K_3[H_2SO_4]^2} \qquad ...(v)$$

For a given kinetic run, the concentration of sulphuric and acid oxalic acid will be constant. The equation (v) may be written as follows :

$$-\frac{d[Ce(IV)]}{dt} = k[Ce(IV)] \quad ...(vi)$$

Which is experimental rate equation for disappearance of Ce(IV) ion.

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Solid State Studies on Polymerization and Depolymerization of 12-Heteropoly Molybdochromate (III)

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THE present communication deals with the preparation and characterisation of a new condensation inorganic polymer, $K_5[CrMo_{12}O_{40}]\ 36H_2O$. The oxidation state of chromium has been established by E.S.R. method and the studies on thermal depolymerization of the compound has also been carried. Of condensation inorganic polymer[1], very few references on heteropoly molybdochromate[2] are found in the literature. The present note is an attempt towards that line.

To 80 ml. of M/15 potassium dichromate solution, 50 ml. of M/10 aqueous solution of molybdic acid and 10 ml. of '20 volume' hydrogen peroxide solution was gradually added with constant stirring at a controlled temperature of 80° in a thermostat. The stirring was continued for two hours and then the solution was left for three days in vacuum, when orange coloured needle shaped crystalline compound came out which was recrystallised thrice from hot water. The analysis of the compound was carried out by usual chemical and colorimetic methods. Estimation of potassium has also been corroborated by flame photometric method. (Found : K, 7.10 ; Mo, 42.65 ; Cr, 1.80 ; H, 2.50% Cald. for $K_5[CrMo_{12}O_{40}]36H_2O$: K, 7.25; Mo, 42.87; Cr, 1.93; H, 2.67%). Hydrogen has been estimated by element estimation method and molybdenum has been determined by colorimetric method[3]. From the analytical data, the molecular formula of the compound, as per Keggin's view[3], comes out to be $K_5[CrMo_{12}O_{40}]\ 36\ H_2O$, which may be named as 12-heteropoly molybdochromate.

Molecular Weight Determinations : The molecular weight of the polymeric compound has been determined accurately by X-ray crystal diffraction technique[4]. A single crystal of the compound was mounted along its longer dimention : a axis. By taking rotation and Weissenberg X-ray diffraction photographs, the values of unit cell dimentions were found to be $a=11.62$, $b=26.12$, $c=8.62$ Å & $\alpha=\beta=\gamma=90°$, volume per unit cell 'V' was calculated to be 2616·294 Å^3. No. of molecules per unit cell 'Z'=2. Pycnometric measurement gives the observed density $\rho_{obs.}=3.38\ gml^{-1}$. From the relation, $\rho_{obs}=1.66\ M.Z/V$, the molecular weight 'M' of the compound comes to 2664 against the calculated value 2687.

Measurement of Oxidation State of the Heteroatom : The E.S.R. spectra of the compound were recorded on the powdered sample, using varian 4502-15 E.S R. spectrometer system, operating at 100 Kcps field modulation. The X ray band spectum shows only one line at 3500 gauss, $g_{eff.}=1.9919$ (77°K). The diluted sample e.s.r. spectra has several shoulders which pemit a reasonably accurate assessment of D value being 0.16 cm^{-1} and λ being 0.1211. There is strong distortion from O_h symmetry. Obviously from the comparative chart, $g_{eff.}$ value of the compound indicates chromium to be present in +3 oxidation state having d^3 configuration. The relative spin concentrations were determined by multiplying the peak-to-peak hight of the derivative signal by the square of the maximum slop width and absolute concentration were estimated by comparision with standard sample[5].

Thermal Depolymerisation : The thermal depolymerization of the compound has been studied in the light of the investigations made by West and Andrieth[6] and by Babad-Zakhryapin[7] on a few heteropolytungstic acids. The apparatus used for this purpose was that described by Ray and Sinha[8] with continuous pumping the depolymerised product, followed by successive weighing using a thermogravimetric balance and estimations at some stages. The dissociation[4] of the compound was observed at 80° under reduced pressure when twelve molecules of water were lost. Of the rests, seven water molecules remained intact in the crystal latice till 290°, above which they were completely removed. When the temperature was raised still higher, then nearly at 450°, the compound was broken as a whole into the basic units of lower oxides of molybdenum and chromium which have been confirmed by analysis. So the thermal stability of 12-heteropoly molybdochromate is 450°±5°.

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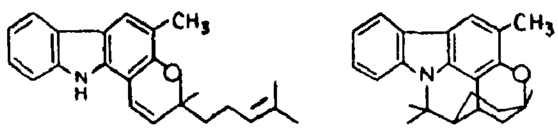
Mahanimbine and Murrayazoline from *Murraya exotica* Linn.* (Syn. *Murraya paniculata*)

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ON chemotaxonomic considerations, we were interested to examine different species of the genus *Murraya* as one of the species *Murraya koenigii* Spreng. is the richest source of carbazole alkaloid[1]. *Murraya exotica* has been the subject of numerous investigations[2] but so far no carbazole alkaloid has been reported from it. We, now report two carbazole alkaloids, mahanimbine, $C_{23}H_{25}NO$(I), m.p. 94° and murrayazoline $C_{23}H_{25}NO$(II), m.p. 260° from it.



(I) (II)

The neutral fraction of the petroleum ether extract of the stem bark of *Murraya exotica* gave in a very poor yield a crystalline carbazole derivative m.p. 94°. The IR spectrum of the compound (I) showed the presence of —NH and an aromatic system. (ν_{max}^{Nujol} 3359, 1647, 1613, 1575, 1493 cm^{-1}). The UV spectrum of (I) (ν_{max}^{EtOH} 223, 239, 188, 330, 343 nm with log ε 4.55, 4.06, 4.61, 3.90, 3.42) was superimposable with that of mahanimbine[3]. The compound was identified as mahanimbine by direct comparison (T.L.C. and m.m.p.).

From the petroleum ether extract of the powdered leaf of *Murraya exotica* a crystalline colourless neutral Hot-II nitrogenous homogenous compound, m.p. 260°, $[\alpha]_D$ was isolated. The IR spectrum of the compound (II) showed the presence of an aromatic system (ν_{max}^{Nujol} 1622, 1590, 1480, 1375, 1368, 852, 873 cm^{-1}). The UV spectrum (ν_{max}^{EtOH} 245, 307 nm with log ε 4,69, 4.16) was suggestive of the presence of 2-methoxy carbazole chromophore. The physical and analytical data were suggestive of the identity of the compound with murrayazoline which was confirmed by the direct comparison with pure specimen of murrayazoline[4] (mmp., TLC and UV, IR).

Though the yield of the two compounds are very poor, their occurrence in both the species (*M.exotica* and *M. koenigii*) is taxonomically interesting.

Acknowledgement

The authors thank Prof. S. K. Mukherjee, Director and Professor A. Sen, Head of the Department of Chemistry for their interest in the work.

*Part 39 in the Series of Chemical Taxonomy. Part 38. S. Roy, R. Guha and D.P. Chakraborty, *Chem. & Ind.* (in press)

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Chemical Constituents of *Pteris longifolia*

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Manuscript received 24 May 1977, accepted 3 October 1977

EARLIER communications[1,2] from this laboratory reported the isolation and characterisation of wallichoside, β-sitosteryl palmitate, β-sitosterol, Pterosin B and Pterosin C from the alcoholic and benzene extract of the rhizomes of an Indian fern, *Pteris wallichiana* (Pteridaceae) respectively. The present report deals with a thorough and systematic chemical investigations of the benzene extract of the whole plant of *Pteris longifolia* (Pteridaceae) as no phytochemical investigations on this fern have so far been reported. This fern and *Pteris biurata*[3] are the only two exceptions in this family so far

reported which did not afford any pterosin or its derivatives.

The air-dried powdered *P. longifolia* was extracted with hot benzene for 18 hrs. The benzene extract was separated into ether soluble and ether insoluble fractions. The latter fraction on column chromatography over silica gel followed by crystallisation from petether-acetone yield a solid, m. p. 88-90°, which was found to be the n tricontanyl ester of hexacosanic acid. ν_{max}^{KBr} 1730, 1170, 730 and 720 cm^{-1}. *MS* m/e 816 (M^+), 420 (M^+—hexacosanic acid, $C_{26}H_{52}O_2$), 396. On hydrolysis with methanolic alkali (5%) gave *n*-triacontanol[4] $C_{30}H_{62}O$, m.p. 90-91°. ν_{max}^{nujol} 3210, 730 and 720 cm^{-1}. *MS* m/e 420 (M^+-H_2O), 392 ($M^+-C_2H_4-H_2O$), 364 ($M^+-H_2O-2\times C_2H_4$) suggesting it to be an alkanol[5] having more than four carbon atoms. (Found : C, 82.2 ; H, 13.9 ; $C_{30}H_{62}O$ requires C, 82.11 ; H, 14.24%) and hexacosanic acid[6], $C_{26}H_{52}O_2$, m.p. 78-82°, ν_{max}^{nujol} 1700, 730 and 720 cm^{-1}. *MS* m/e 396 M^+, 368 (M^+—28).

The ether soluble fraction was separated into acidic and neutral fractions. The acidic fraction on chromatographic separation followed by crystallisatio gave palmitic acid[7], $C_{16}H_{32}O_2$, m.p. 70-71°. ν_{max}^{nujol} 700, and 730 and 720 cm^{-1}. *MS m/e* 256 (M^+), 185, 129, 73, 60.

The neutral fraction was chromatographed over a column of silica gel. Elution with a mixture of petether-benzene (4 : 1) yielded a gummy solid which on crystallisation from chloroform-acetone furnished crystalline β-sitosteryl palmitate[8], $C_{45}H_{80}O_2$, m.p. 85-86°. ν_{max}^{nujol} 1730, 1165, 720 cm^{-1}. *MS m/e* 396 (M^+—palmitic acid), 382, 367, 288, 275, 255, 213, identical (m.m.p. and I.R.) with an authentic specimen. On hydrolysis this ester yielded β-sitosterol[9], m.p. 136-138°, acetate, m.p. 126-128°, and a fatty acid which was identified (m.m.p. and I.R.) as palmitic acid, $C_{16}H_{32}O_2$, m.p. 65-70° Elution of the column with petrolbenzene (3 : 2) afforded a petether benzene solid which on crystallisation from chloroform-methanol furnished β-sitosteryl acetate $C_{31}H_{52}O_2$, m.p. 126-128°, identical (m.m p. and I.R.) with an authentic sample. Further elution of the column with petether-benzene m.p., (2 : 3) gave β-sitosterol. m.p.p. 136-138°, acetate, m.p. 126-128°, identical with an authentic specimen.

Acknowledgement

The authors are highly indebted to Prof. P. Sengupta, Head, Department of Chemistry, Universitry of Kalyani, for his guidence and encouragement, Dr. S. C. Pakrashi, Assistant Director, Indian Institute of Experimental Medicine, Calcutta, for spectral measurements and University Grant Commission, New Delhi for financial assistance to one of them (U. S.)

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Obituary

Devadas Devaprabhakara (1932-1978)

Devadas Devaprabhakara was born as the younger son of a parsih priest in Bangalore on November 12, 1932. He had his earlier education in Mysore State and received the Ph.D. degree from the University of Texas. He joined IIT, Kanpur in 1964 where he was Professor of Chemistry at the time of his passing away on January 12, 1978.



Deva—as invariably every one called him—was a special type of person, a rare blend of humility, erudition, dedication, and true Christian spirit. His unruffled exterior covered a turbulent mind which always yearned for lofty ideals in life. He was an outstanding teacher and his research work earned for him a permanent place amongst the national and international scientists. He has been the recipient of many academic awards of which mention may be made of Bhatnagar award, the Basudev Banerjee memorial award of the Indian Chemical Society and Fellowship of the Indian Academy of Sciences.

His work related principally to novel molecular frameworks that either incorporated a strain factor such as those present in cyclic allenes and medium ring dienes or a boron-carbon bond. His research on hydroboration and other addition reactions of acyclic and cyclic 1,2 and 1,n dienes has brought to light many novel and subtle facets associated with stereochemistry, conformation, and reaction mechanism of these systems and has also led to the delineation of novel reaction pathways and to the discovery of new and useful reactions.

It is in the area of human relations that Deva scored over most others. All those who came under his sphere of influence received in abundance his affection and concern. His life was dedicated to the study of bonds and of these he held the personal ones with utmost reverence. Nothing came easy to Deva. He always earned whatever he received. The very many perturbations that fate imposed on him failed to shake his belief in human values. His ceaseless endavours to usher a new order in the practice of organic chemistry will surely inspire many generations to come.

He has left behind his wife, two children, and countless friends and admirers to mourn his death.

S. Ranganathan

Obituary

Dr. N. C. Sogani

Dr. Navin Chandra Sogani, passed away on January 16, 1978 due to sudden heart failure. He was born in a respectable family on August 17, 1923 at Ajmer (Rajasthan). He graduated in 1944 and passed M. Sc. Examination in Chemistry in 1946 from Banaras Hindu University. After serving at few places he joined as Lecturer in Chemistry, Govt. College, Ajmer in 1949. Later he proceeded to National Chemical Laboratory, Poona to work for his Ph.D. degree with Professor S. C. Bhattacharya (now Director, Bose Institute, Calcutta). He was awarded Ph.D. degree in 1956 from Agra University. He was so much inspired by Professor Bhattacharya that he continued his research work after returning to Govt. College, Ajmer. Inspite of very meagre facilities there one candidate got Ph.D. degree under his supervision.

Dr. Sogani joined in 1959 as Assistant Professor in Analytical Chemistry at Indian Agricultural Research Institute, Delhi. After serving a year there he preferred to join as Lecturer in the Department of Chemistry, University of Rajasthan, Jaipur, and became Reader in Inorganic Chemistry in the same department in 1962. He enjoyed this position till his last. In July, 1977 he was requested by the University to become the Principal, University Maharaja's College, Jaipur which he accepted and died in office on January 16, 1978. Inspite of this added administrative responsibility he continued his teaching and research activity till his demise. Dr. Sogani had a great reputation as a teacher and a research supervisor. Those who came in his contact remember well his masterly exposition of coordination chemistry in the most simplest manner. Among his colleagues and students he was universally respected for his depth of knowledge in the subject. He was loved by his students for his advice and ever-helping attitude.

He had done extensive work in the field of analytical and coordination chemistry and published about 125 research papers in Indian and foreign journals. He was reciapient of Cooper Memorial Medal, awarded by the Institution of Chemists (India), for his best research paper in 1971. His name will be remembered with hydroxytriazenes which he used as selective and specific analytical reagent for palladium. His other interests were in the studies of metal complexes of hydroxamic acids and sulphur containing ligands. About 20 candidates got their Ph.D. degree under his guidance and supervision. He was Life Member of the Indian Chemical Society.

In his death the country has lost an outstanding veteran teacher and chemist of repute.

C. S. Bhandari

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A Study of the Complex Compounds of N-Benzenesulphonyl Glycines with Some Metal Ions : Part (XXIII). Potentiometric Study of *Bis*-N-Benzenesulphonyl-L-Cysteinato Mercury(II)

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Manuscript received 29 September 1977, accepted 7 December 1977

Bis-N-Benzenesulphonyl-L-cysteinato mercury (II) viz. $Hg(RH_2)_2$ and its disodium salt $Na_2Hg(RH)_2$ H_2O C_2H_5OH (where RH_3 = N-benzenesulphonyl-L-cysteine, NBSC) have been isolated. Stepwise acid dissociation constants of $Hg(RH_2)_2$ have been determined potentiometrically in 1:1 water-ethanol at a constant ionic strength ($\mu = 0.50$) and at $30 \pm 0.5°$. The values of pk_4^*, pk_3^*, pk_2^* and pk_1^* have been found to be 3.13, 4.19, 10.49 and 11.54 respectively. With a dilute solution of Cu(II), $Hg(RH_2)_2$ gives a deep blue colouration in 1:1 aqueous-ethanol at $pH \approx 2.5$-3.0 and a greenish yellow colouration at $pH \approx 9.5$-10.0 indicating some interesting complex formation.

In previous communications[1,2] potentiometric and rotatometric study of the complex formation of the ligand N-benzenesulphonyl-L-cysteine (NBSC or RH_3) (I), with Zn(II) have been described, when NBSC acted as a tridentate ligand, being biprotic at lower pH values and triprotic at higher pH values.

$$C_6H_5SO_2\ NH\ \underset{\displaystyle COOH}{\underset{|}{CH}}CH_2SH$$

(I)

In the present communication the authors describe the isolation of the complex *bis*-N-benzenesulphonyl-L-cysteinato mercury (II) viz. $Hg(RH_2)_2$ and its disodium salt $Na_2Hg(RH)_2$ H_2O C_2H_5OH when the ligand NBSC has been found to act as a bidentate one. Stepwise acid dissociation of $Hg(RH_2)_2$ have been followed potentiometrically in 1:1 water-ethanol maintaining a constant ionic strength ($\mu = 0.50$) at $30 \pm 0.5°$. $Hg(RH_2)_2$ has been found to act as a tetrabasic acid and four successive acid dissociation constants have been found out by the method of Irving and Rossotti[3].

Experimental

Materials : (a) N-Benzenesulphonyl-L-cysteine (RH_3) was obtained by following the usual procedures[1,4].

(b) Bis-*N-Benzenesulphonyl-L-cysteinato mercury (II)* -*Hg* $(RH_2)_2$

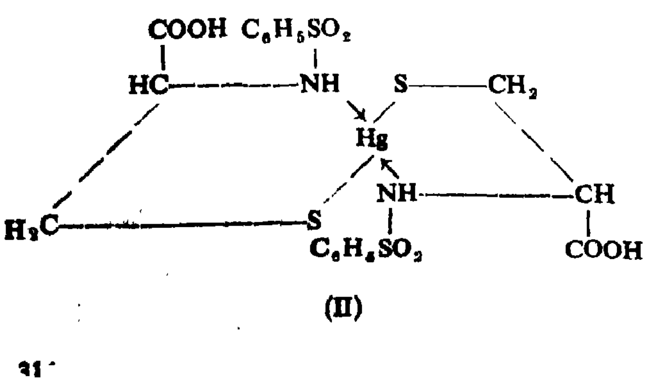
About 50 ml of an aqeuous solution of 1.5 g of $HgCl_2$ (1 mole) was added with stirring to 150 ml of a warm solution of 3g of NBSC (2 moles). $Hg(RH_2)_2$ separated as a white sticky mass which became granular after half-an-hour. The solid was filtered and washed with water. It was then dissolved in ethanol, norited and crystallized from aqueous ethanol. The white shining crystals of $Hg(RH_2)_2$ were collected and dried in a vacuum desiccator over H_2SO_4 and KOH ; and found m.p. 187°. The compound on analysis furnished Eqv. wt. 362 ; Hg, 27.61% ; Calc. for $Hg(RH_2)_2$: Eqv. wt., 360 (dibasic) ; Hg, 27.84%. The compound is soluble in ethanol, acetone, dioxan and insoluble in water. A deep blue solution was obtained on adding a dilute solution Cu(II) sulphate to a solution of $Hg(RH_2)_2$ in 1:1 aqueous-ethanol at $pH \approx 2.5$-3.0, the colour changed to greenish yellow on raising the $pH \approx$ 9.5-10.0. This may probably be due to some remarkable complex formation of $Hg(RH_2)_2$ as a ligand with Cu(II). More detailed study is being made on this colour reaction.

(c) *Disodium*-bis-*N-benzenesulphonyl—L—cysteinato mercury (II)* $Na_2Hg(RH)_2$ H_2O C_2H_5OH

An aqueous suspension of $Hg(RH_2)_2$ (1 mole) was treated with an aqueous solution of NaOH (2.1 moles), stirred, when all $Hg(RH_2)_2$ passed into solution ($pH \approx$ 7.5). The solution was norited, filtered, the filtrate was evaporated to a small volume in a vacuum desiccator over H_2SO_4 and this concentrated solution was treated with an excess of ethanol when a white compound separated. This was filtered, washed with ethanol and finally with a little (1:1) aqueous-ethanol, dried in a vacuum desiccator over H_2SO_4 and KOH. Found : Na, 5.54 ; Hg, 24.16 ; loss at 105°, 7.67% ; Calc. for $Na_2Hg(RH)_2.H_2O.C_2H_5OH$: Na, 5.55 ; Hg, 24.21 ; loss at 105° ($H_2O + C_2H_5OH$), 7.72%. The compound gave a positive iodoform test supporting the presence of C_2H_5OH.

IR spectra (KBr phase) of $Hg(RH_2)_2$ and $Na_2Hg(RH)_2.H_2O.C_2H_5OH$ were recorded and tentative assignments[4] of some important vibrations were made in Table 1, which also contains some such ir data[6] of RH_3 and KRH_2 for comparison.

The disappearance of S-H stretching frequency at 2597-2532 cm^{-1} in this complex support the formation of Hg-S bonds. The ligand RH_3 and the complex $Hg(RH_2)_2$ showed the C=O stretching band (1730-1724 cm^{-1}) suggesting the presence of -COOH group in $Hg(RH_2)_2$ as in RH_3. This band however disappeared in both the cases on salt formation with consequent appearance of antisymmetric and symmetric COO^- bands at 1585-1575 cm^{-1} and 1410-1408 cm^{-1} respectively. The red shifts of the $-SO_2N<$ band II at 1342 cm^{-1} in complex indicate the formation of Hg-N bonds. Thus the following structure (II) may be tentatively suggested for $Hg(RH_2)_2$:



(II)

TABLE 1—SOME IR BANDS OF INTEREST AND ALONG WITH THEIR TENTATIVE ASSIGNMENTS

Compounds and their i.r. bands in Cm^{-1}				Tentative assignments
RH_3[6]	KRH_2[6]	$Hg(RH_2)_2$	$Na_2Hg(RH)_2.H_2O.C_2H_5OH$	
3257-3175 vs 3077-2857 s	3333-3030m	3250 vs 3070 s sh	3500-3400 s br 3240s br	H-bonded N-H, O-H stretches
2597 m	2532 w	—	—	S-H, stretches
1724 vs	—	1730 vs	—	Due to COOH
—	1575 vs	—	1585 vs	Antisymmetrical COO^- stretches
—	1408 m	—	1410 m	Symmetrical COO^- stretches
1342 vs	1342 vs	1310 vs	1295 m	$-SO_2N<$ band II
1163 vs	1163 vs	1155 vs	1145 s	$-SO_2N<$ band I

sh=shoulder, vs=very strong, s=strong, m=medium, br=broad, w=weak.

Potentiometric Determination of successive acid dissociation constants (k_4^*, k_3^*, k_2^*, and k_1^*) of $Hg(RH_2)_2$:

Procedure : (i) Potentiometric titrations of 50 ml solutions in 1:1 water ethanol of composition (a) 0.02*M* $HClO_4$ and (b) 0.02*M* $HClO_4$ + 0.005*M* $Hg(RH_2)_2$, with 0.12*M* NaOH in 1:1 water-ethanol of desired ionic strength were made using a Cambridge *p*H-Meter (Portable Type) having a glass electrode (1-13 *p*H range) in conjunction with a saturated calomel electrode connected to the cell by means of an agar 2M-$NaNO_3$ bridge. The *p*H-Meter was calibrated with aqueous sodium-hydrogen phthalate and borax buffer solutions with due temperature corrections. *p*H measurements were made after attainment of equilibrium at the desired temperature (30±0.5°). Ionic strength of the medium was maintained constant throughout by adding requisite amount of $NaClO_4$.

(ii) Titration curves were obtained by plotting the *p*H-Meter reading (*p*H) against the volume of alkali added at various stages of the titrations (Fig. 1). The average number ($\bar{n}_H$) of protons bound to the complex ion $Hg(R)_2^{4-}$ were calculated using the relation[5]

$$\bar{n}_H = Y - [(v'' - v')(N^\circ + E^\circ)/T_L]/(v^\circ + v')$$

where v°, E° and T_L are the initial volume of the mixtures, initial concentrations of $HClO_4$ and $Hg(RH_2)_2$ respectively, N° is the concentration of the titrant NaOH solution. v' and v'' are the volumes of the titrant alkali required to get the same *p*H meter readings in the titrations of solutions (a) and

(b) respectively. In the present case $Y=4$, as because four equivalents of alkali were consumed by $Hg(RH_2)_2$ for complete neutralisation (Fig. 1). $\bar{n}_H$ values were plotted against pH meter reading (pH)

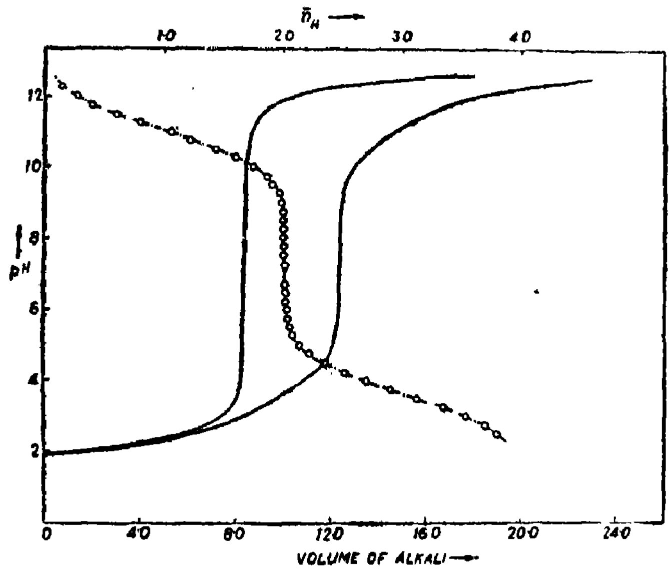


Fig. 1. Titration curves ———; of (a) 0.02M $HClO_4$, (b) 0.025M $HClO_4$ + 0.005M $Hg(RH_2)_2$, with 0.12M NaOH solution. $\bar{n}_H$ (pH) plot ; experimental point ; O–O ; calculated curve, —.—.—

Results and Discussion

Consumption of four equivalents of alkali by $Hg(RH_2)_2$ suggests four successive steps of its acid dissociation as represented by the equilibria (1), (2), (3) and (4).

$$Hg(RH_2)_2 \rightleftharpoons H^+ + Hg(RH_2)(RH)^- \quad \ldots \quad (1)$$

$$Hg(RH_2)(RH)^- \rightleftharpoons H^+ + Hg(RH)_2^{2-} \quad \ldots \quad (2)$$

$$Hg(RH)_2^{2-} \rightleftharpoons H^+ + Hg(RH)(R)^{3-} \quad \ldots \quad (3)$$

$$Hg(RH)(R)^{3-} \rightleftharpoons H^+ + Hg(R)_2^{4-} \quad \ldots \quad (4)$$

for which the successive acid dissociation constants are k_4^*, k_3^*, k_2^* and k_1^* respectively. The average number ($\bar{n}_H$) of protons bound to the complex $Hg(R)_2^{4-}$ ion is given by the relation (5)

second acid dissociation constants k_4^* and k_3^* respectively were evaluated from graphical solutions (Fig. 2)

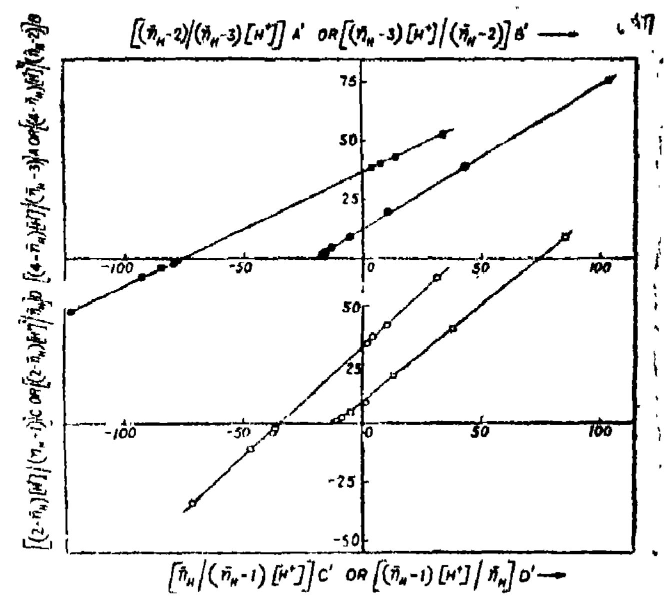


Fig. 2. Linear plots for evaluation of k^*_4 and k^*_3 of $Hg(RH_2)_2$ based on equations (6) ; ■—■, A = 5 × 10⁴, A′ = 5 × 10⁻⁸, (7) ●—●, B = 2.5 10⁸, B′ = 3 × 10⁸ and of k^*_2 and k^*_1 based on equations (8), ⊙—⊙, C = 1 × 10¹⁹, C′ = 1 × 10⁻¹⁰; (9) □—□, D = 1 × 10¹⁹, D′ = 4 × 10¹⁹.

of the equations

$$[H^+](4-\bar{n}_H)/(\bar{n}_H-3)=k_4^*+k_4^*k_3^*(\bar{n}_H-2)/(\bar{n}_H-3)[H^+] \quad (6)$$

$$[H^+]^2(4-\bar{n}_H)/(\bar{n}_H-2)=k_4^*k_3^*+k_4^*[H^+](\bar{n}_H-3)/(\bar{n}_H-2) \quad (7)$$

and the third and fourth acid dissociation constants k_2^* and k_1^* respectively from graphical solution of the equations

$$[H^+](2-\bar{n}_H)/(\bar{n}_H-1)=k_2^*+k_2^*k_1^*\,\bar{n}_H/(\bar{n}_H-1)[H^+] \quad (8)$$

$$[H^+]^2(2-\bar{n}_H)/\bar{n}_H=k_2^*k_1^*+k_2^*[H^+](\bar{n}_H-1)/\bar{n}_H \quad (9)$$

all of which can be derived from equation (5) assuming $[Hg(RH)(R)^{3-}]$ and $[Hg(R)_2^{4-}]$ negligible at pH ≤ 6

$$\bar{n}_H=\frac{4[Hg(RH_2)_2]+3[Hg(RH_2)(RH)^-]+2[Hg(RH)_2^{2-}]+[Hg(RH)(R)^{3-}]}{[Hg(RH_2)_2]+[Hg(RH_2)(RH)^-]+[Hg(RH)_2^{2-}]+[Hg(RH)(R)^{3-}]+[Hg(R)_2^{4-}]} \quad \ldots \quad (5)$$

The $\bar{n}_H$ (pH) plot (Fig. 1) shows that $\bar{n}_H$ remains practically unchanged (≃2) on varying the pH in the region 6-9 which suggests that the most predominant species in solution at this pH range is the complex $Hg(RH)_2^{2-}$ ion and the second and third acid dissociation steps are independent of each other. There is an appreciable interval of pH between the completion of the second step (2) and the commencement of the third step (3). The plot also shows that there is overlapping of the first step (1) with second step (2) and of the third step (3) with the fourth step (4). Hence the first and values while $[Hg(RH_2)_2]$ and $[Hg(RH_2)(RH)^-]$ negligible at pH ≥ 9 values. The values of pk_4^*, pk_3^*, pk_2^* and pk_1^* have been stated in Table 2 along with standard deviation (σ) calculated by usual procedure[7]. The limits of error[8] were also found out from a comparison of the experimental $\bar{n}_H$ (pH) plot with a calculated one (Fig. 1). Results are stated in Table 2.

The first two steps of acid dissociation involve the successive proton ionisation of two-COOH groups and the third and fourth steps involve deprotonation of two

TABLE 2—RESULTS OF POTENTIOMETRIC TITRATION OF $Hg(RH_2)_2$ IN 1 : 1 WATER-ETHANOL (μ=0.50) AT 30±0.5°

pk_4^*	pk_3^*	pk_2^*	pk_1^*
3.13±0.03	4.19±0.03	10.49±0.03	11.54±0.03

(σ) = ±0.018 in the range ($0.1 < \bar{n}_H < 3.8$)

sulphonimido -SO_2NH- groups. It has been found earlier that the acidity of the hydrogen of -SO_2NH- group is enchanced when nitrogen of this group coordinates a metal ion[9]. In *bis*-N-benzenesulphonyl glycinato or β-alaninato mercury(II) containing the unit [HgN_2O_2] both the imidohydrogen atoms were lost at low *p*H values[10,11]. The low acidity ($pk_2^* =$ 10.49, $pk_1^* = 11.54$) of the imido hydrogens in the case of $Hg(RH_2)_2$ containing the unit [Hg S_2N_2] (structure II) is probably due to the fact that soft Hg(II) forms its best bonds with sulphur which is definitely softer than nitrogen. As a result of this, the bonds between mercury(II) and nitrogen are not as strong as to facilitate easy ionisation of the imido hydrogens as have been found in the other cases[9-11] where the metal ions definitely formed stronger bonds with nitrogen atoms of the -SO_2NH-groups.

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Potentiometric Studies of Some Bivalent Metal Chelates of 3-Aldehydosalicylic Acid-Aniline Schiff Base

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Complexation equilibria of metal complexes of UO_2^{++}, Cu^{++}, Ni^{++}, Co^{++} and Mn^{++} with 3-Aldehydosalicylic acid-aniline (abbriviated 3.ASAA) have been carried out potentiometrically. The stability constants of these chelates were determined in 30/70 (v/v') dioxane-water medium by Calvin-Bjerrum titration technique[1,2] at 25° in a medium of 0.2*M* ionic strength.

THE chelating properties of 3.ASAA with some bivalent metals have been studied. But little attention has, however, been paid to determine the stability constants of these complexes of this compound. In the present communication the metal-ligand stability constants were determined by using Irving-Rossotti method[3]. The Job's method[4] was applied to establish the composition conductometrically.

Materials

All chemicals used were of analytical grade. The dioxane[5] and sodiumhydroxide[6] free from carbondioxide were prepared. 0.1*M* perchloric acid was prepared by titrating it against standard NaOH. 2.0*M* sodiumperchlorate was prepared in double distilled water.

For potentiometric studies metal sulphates were used, while acetates of metals were used for separation of solid complexes.

Conductometric measurements were done with the help of Elico-conductivity bridge model. CM-82.

A Metrohm *p*H meter E-350 A with a wide range glass electrode in conjugation with a calomel electrode was used and calibrated at two *p*H ; at 4.01 *p*H with potassium hydrogen phthalate and at 7.0 *p*H with potassium hydrogen phthalate and sodiumhydroxide buffers. All titrations were performed in 100 ml pyrex beaker equipped with stirrer. Quickfit glass assembly was used for the preparation of ligand.

Experimental and Results

Preparation of ligand : The ligand was prepared in the laboratory[7,8] and was analysed for its purity before use.

Composition of the complexes : Job's method[4] was employed to establish the composition of the complexes conductometrically. The results showed that complexes contain metal and the ligand in the ratio of 1:1. All measurements were done in 50% aqueous ethanol medium.

Potentiometric titrations : The following solutions were titrated separately (I) free $HClO_4$, (II) free $HClO_4$+Ligand and (III) free $HClO_4$+Ligand+Metal. The ratio between metal and ligand was kept 1:6 to fulfill the maximum co-ordination number of the corresponding metal ions. The ionic strength was maintained at 0.2*M* by the addition of an appropriate amount of 2*M* $NaClO_4$ solution.

The titrations were carried out in an inert atmosphere by bubbling oxygen free nitrogen gas through the titration assembly containing the electrode.

The values of $\bar{n}_A$, $\bar{n}$ and *pL* were calculated by employing Irving-Rosssotti equation[9].

Calculation of stability constants : From the titration curve using the solution (I) and (II) $\bar{n}A$ values of the varius *p*H values were calculated. The formation curve of proton-ligand curve was obtained by plotting a graph between $\bar{n}A$ and *p*H. The values $\log K_1H$ and $\log K_2H$ were determined by using various computational methods[8]. The values are reported as under (Table 1.)

TABLE 1—PROTON-LIGAND STABILITY CONSTANTS OF 3 ASAA

Method	$\log K_1H$	$\log K_2H$	$\log \beta_2H$
Interpolation at various $\bar{n}A$ values	10.10	4.05	14.15
Interpolation at half $\bar{n}A$ values	10.08	4.05	14.13
Mid Point Method	10.08	4.12	14.20
Mean	10.08	4.08	14.16

From the titration curve using the solution (II) and (III) $\bar{n}$ values of the metal chelates were determined at various *p*H values. From this data the corresponding *pL*

were then calculated. The $\bar{n}$ values plotted against the corresponding pL were to get the formation curves of the metal complexation equilibria. The approximate values of log K_1 were directly noted down from the curves and tabulated in Table 2.

TABLE 2—STABILITY CONSTANTS OF METAL LIGAND CHELATES

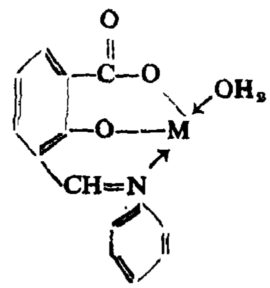
Metal	log K_1
UO_2^{++}	6.95
Cu^{++}	5.64
Ni^{++}	5.26
Co^{++}	5.15
Mn^{++}	5.04

Discussion

The metal ligand curve has been found to be well separated from the titration curve which indicates that the liberation of protons is due to chelation. Possibility of metal ions to hydrolyse has been ignored as the complex is found to be stable in the pH range studied.

The stability constants of metal complexes of this ligand show the order $UO_2 > Cu > Ni > Co > Mn$. This confirms the validity of Irving-Williams[10] order for these complexes.

It is evident from the conductometric and potentiometric studies that this ligand forms 1:1 complexes. The Schiff base behaved as tridentate ligand with these metals and the tentative structure is ascertained as :



$M = UO_2^{++}, Cu^{++}, Ni^{++}, Co^{++}, Mn^{++}$

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Potentiometric Studies on Quaternary Complexes of Dioxouranium(VI) with Dibasic Acids

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Formation of 1:1:1:1 quaternary complexes of dioxouranium(VI) ion with dibasic acids such as oxalic (OX), malonic (MALN), phthalic (PHA) and maleic (MA) acids has been inferred from pH metric studies and the stability constants of the resulting species have been evaluated.

As reported in the literature[1,2] uranyl ion forms stable mixed ligand complexes in preference to simple binary complexes on the addition of more than one ligand. Thus the hydrolysis and polymerisation reactions of the simple 1:1 binary complexes exhibited on account of the available coordination sites of the central metal ion are postponed. The review of the literature reveals, although enough amount of work has been carried out on the ternary systems involving dioxouranium(VI) ion, only a few references are available on the quaternary systems[3]. It has, therefore, been considered of interest to carry out potentiometric investigations on some quaternary systems such as UO_2-L-L′-L″ where L, L′ and L″ are the different dibasic acids. The results of these investigations are presented in this communication.

Experimental

All the chemicals used were of BDH Analar grade. The stock solution of uranyl nitrate $UO_2(NO_3)_2 6H_2O$ was prepared and the metal estimated gravimetrically as U_3O_8.

The ligand solutions were prepared by direct weighing and the concentrations of the solutions were further checked by potentiometric titrations against 0.1 M KOH. The concentrations of the solutions (5×10^{-3} M in metal or ligand), total volume (50 ml) and ionic strength (μ = 0.1 M KNO_3) were always kept constant at the beginning of the titration.

pH measurements were made with Philips precision pH meter (PR 9405 M) with accuracy ±.02 using standard glass (PV 9011) and calomel (PV 9021) electrodes. The instrument was standardized against 0.05 M potassium hydrogen phthalate (pH – 4) at temperature 25±1° before use.

Calculations :

The dissociation constants of dicarboxylic acids were determined by the method of Chaberek and Martell[4] and the formation constant for the quaternary species by the method of Ramamoorthy and Santappa[3] according to which

$$K_{MLL'L''}=\frac{T_M-(1/3[A]X)}{(1/3^4[A]^4X)}\ (T_M=T_L=T_{L'}=T_{L''})$$

where
$$[A]=\frac{(2T_L+2T_{L'}+2T_{L''}-T_{OH}-[H])}{\dfrac{6[H]^2}{K_1K_2+K_1'K_2'+K_1''K_2''}+\dfrac{3[H]}{K_2+K_2'+K_2''}},$$
$$(2T_L+2T_{L'}+2T_{L''}=6T_M)$$

$$X=1+\frac{3[H]^2}{K_1K_2+K_1'K_2'+K_1''K_2''}+\frac{3[H]}{K_2+K_2'+K_2''},$$

T_M=Total $[UO_2^{2+}]$, T_L = Total [L], T_L' = Total [L′], $T_{L''}$=Total [L″], [A]=Total free ligand concentration of L, L′ and L″, T_{OH} = base consumed, [H] = free hydrogen ion concentration.

K_1 and K_2, K_1' and K_2' and K_1'' and K_2'' are the first and second dissociation constants of the ligands L, L′ and L″ respectively.

Results and Discussion

The curve representing the potentiometric titration of $UO_2(NO_3)_2$ with KOH is similar to that obtained by Feldman et al[5]., sharp inflection obtained at m= 2.3 (m=moles of alkali added per mole of metal or ligand), being attributed to the formation of species such as $U_2O_5^{2+}$, $U_3O_8^{2+}$, $U_3O_8(OH)^+$, $U_3O_8(OH)_2$ etc.

Curve a representing the titration of 1:1 UO_2(II) dibasic acid system exhibits inflections at m≈2 and m≈4.5. The first inflection at m≈2 (pH – 3.5) may be correlated to the formation of 1:1 UO_2(II)-OX/MALN/PHA/MA complex, which, however, undergoes hydrolysis and polymerisation[5,6] at higher pH. The second inflection at m≈4.5 may, probably, be attributed to the formation of the polynuclear species having U-O-U or U(OH)(OH)U groups.

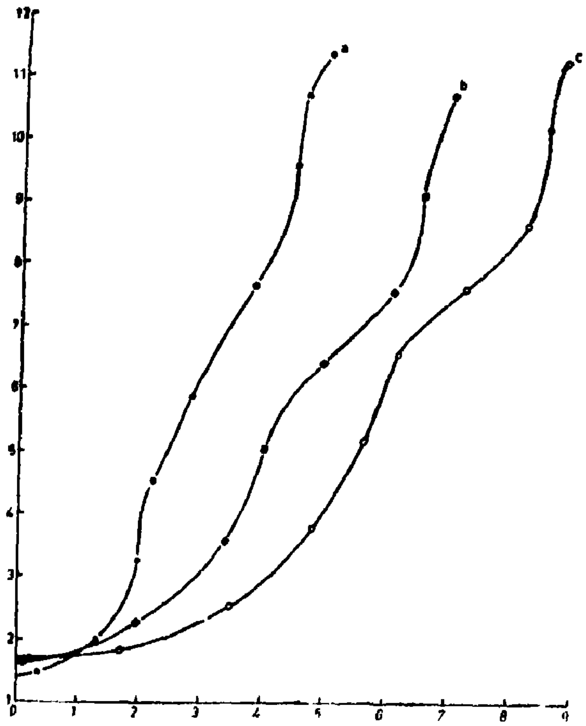


Fig. 1.

The curve b representing the titration of uranyl ion in presence of isomolar amounts of two different acids exhibits inflections at $m \approx 4$ and $m \approx 6.5$. The first inflection may be ascribed to the formation of a 1:1:1 ternary species, whereas the second inflection at $m \approx 6.5$ may be attributed to the hydrolysis and polymerisation of the ternary species.

Curve c represent the titration of 1:1:1:1 quaternary system containing uranyl ion and three different dicarboxylic acid in equimolar ratio. The lowering in pH, non-appearance of a solid phase during the titration in the range of complexation and an inflection at $m \approx 6$ may be attributed to the formation of a 1:1:1:1 UO_2-L-L′-L″ species, which however, undergoes hydrolysis and polymerisation at higher pH, giving a second inflection at $m = 8.5$. The dissociation constants and formation constants are given in table 1 and 2 repectively.

TABLE 1

Ligand	pK_1^a	pK_2^a
Oxalic acid (OXH_2)	1.66	3.90
Malonic acid ($MALNH_2$)	2.75	5.36
Phthalic acid ($PHAH_2$)	2.89	5.04
Maleic acid (MAH_2)	2.23	5.97

TABLE 2

System	*log* $K_{MLL'L''}$
UO_2-OX-MALN-PHA	17.72±0.25
UO_2-OX-MALN-MA	14.05±0.30
UO_2-OX-PHA-MA	11.885±0.16
UO_2-MALN-PHA-MA	16.19±0.19

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Some Mixed Alkoxy Cyano Derivatives of Titanium(IV) and Zirconium(IV)

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The reactions of Ti(IV) and Zr(IV) alkoxides, $M(OR)_4$ (where M=Ti, Zr; R=Et, Pr^i) with pyruvonitrile have been carried out. The products of the type $M(OR)_{4-n}(CN)_n.m\ CH_3COOR$ (where n=1, m=0; n=2, m=0.5; n=3, m=1; n=4, m=1.5 (for M=Ti) or 2 (for M=Zr) have been isolated. The reactions of metal tetracyanide derivatives with isopropanol have also been studied. Attempts have been made to throw light on the nature of these derivatives on the basis of their molecular weights and i. r. spectra.

A number of halide alkoxides of titanium(IV) and zirconium(IV) have been synthesised by the reactions of their alkoxides with acetyl halides[1-6]. The alkoxy isocyanato derivatives of titanium[7] and zirconium[8] have also been synthesized by the reactions of their isopropoxides with acetyl isocyanate. Recently, alkoxy cyanides of niobium(V) and tantalum(V) have been synthesized by the reactions of their alkoxides with pyruvonitrile[9].

In view of these results, it was considered of interest to carry out the reactions of titanium(IV) and zirconium(IV) alkoxides with pyruvonitrile.

Results and Discussions

The reactions of titanium(IV) alkoxides with pyruvonitrile found to be exothermic in nature. Cyclohexane was chosen as a suitable solvent because it forms azeotrope with the esters produced in the reactions. These reactions may be represented by the following general equation:

$$Ti(OR)_4 + nCH_3COCN \longrightarrow Ti(OR)_{4-n}(CN)_n.m\ CH_3COOR + (n-m)\ CH_3COOR$$

(where n=1, m=0; n=2, m=0.5; n=3, m=1; n=4, m=1.5 and R=Et or Pr^i).

The monocyano derivative, $Ti(OPr^i)_3(CN$ is semisolid in nature and is soluble in common organic solvents while other alkoxycyano derivatives are solids, soluble in acetone and insoluble in other common organic solvents. The tetracyanide derivative $Ti(CN)_4.1.5CH_3COOPr^i$ is soluble even in acetone.

Molecular weight determination of $Ti(OPr^i)_3CN$ shows a complexity of the order of 2.5 in refluxing benzene. Molecular weights of di-and tri-cyano derivatives measured in acetone suggested a tendency of slow dissociation to a monomeric form.

As depicted by the infra red spectra the alkoxy cyano derivatives associate mainly through alkoxy bridges but weak association through cyanide bridges is also indicated. The lower solubility tendency of the higher cyano derivatives thus appears to be mainly due to more ionic character of the bonds coupled with their weak association in the solid state through cyanide bridges (which tend to get broken in polar solvents like acetone).

All the alkoxy cyano derivatives of titanium on being heated under reduced pressure disproportionate to give their alkoxides.

The reactions of crystalline $Zr(OPr^i)_4.Pr^iOH$ with pyruvonitrile in different molar ratios under refluxing conditions gave products with CN : Zr ratios lower than expected. This might be due to the competitive reaction tendency of the adduct with pyruvonitrile at higher temperature. The reactions were, therefore, repeated at the room temperature. On leaving a equimolar mixture of $Zr(OPr^i)_4.Pr^iOH$ and CH_3COON overnight, $Zr(OPr^i)_3(CN).Pr^iOH$ could be obtained. However, the reaction in 1:4 molar ratio yielded only the tri-cyano product, $Zr(OPr^i)(CN)_3.CH_3COOPr^i$.

In view of the complications caused by the isopropanol, crystalline $Zr(OPr^i)_4Pr^iOH$ was first refluxed with cyclohexane and the adduct isopropanol was removed azeotropically. The required amount of pyruvonitrile was then added in different molar ratios and the reaction mixtures were refluxed. All these reactions, can be represented as follows :

$$Zr(OPr^i)_4 + nCH_3COCN \longrightarrow Zr(OPr^i)_{4-n}(CN)_n.m\ CH_3COOPr^i + (n-m)CH_3COOPr^i$$

(where n=1, m=0; n=2, m=0.5; n=3, m=1; n=4, m=2).

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The mixed isopropoxy cyanides as well as *zirconium tetracyanide* are insoluble in common organic solvents and, *therefore, their molecular weights* could not be determined.

In view of the observed differences in the reactivities of titanium and zirconium tetrahalides with alcohols, it was considered worthwhile to study the reactions of these metal tetracyanides also with isopropanol. The reaction of titanium tetracyanide. $Ti(CN)_4.1.5\ CH_3COOPr^i$, with isopropanol gives the dicyanide diisopropoxide of titanium :

$$Ti(CN)_4.1.5\ CH_3COOPr^i + 2Pr^iOH \rightarrow Ti(OPr^i)_2(CN)_2 \\ (excess) + 1.5CH_3COOPr^i + 2HCN \uparrow$$

No coordination of either ester or isopropanol to titanium dicyanide diisopropoxide was observed. Similarly, titanium tetrabromide containing isopropyl acetate of addition, has also been reported to react with isopropanol to give the dibromide diisopropoxide[8] :

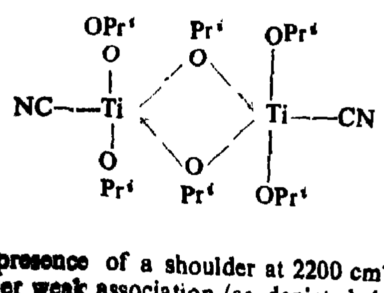
$$TiBr_4.CH_3COOPr^i + 2Pr^iOH \rightarrow TiBr_2(OPr^i)_2 \\ + CH_3COOPr^i + 2HBr.$$

On refluxing $Zr(CN)_4.2CH_3COOPr^i$ with isopropanol, the analysis of the final products obtained corresponds to an equimolar mixtures of di- and tri-cyanide derivatives of zirconium(IV) isopropoxides :

$$2Zr(CN)_4.2CH_3COOPr^i + 7Pr^iOH \rightarrow Zr(OPr^i)_2.(CN)_2. \\ 2Pr^iOH + Zr(OPr^i)(CN)_3.2Pr^iOH + 4CH_3COOPr^i \\ + 3HCN \uparrow$$

This rection also is similar to those of zirconium tetrachloride and bromide.

Mono cyano titanium triisopropoxide shows a band at about 2175 cm^{-1} and a weak shoulder at about 2200 cm^{-1} in its infrared spectrum. In view of only one dominant peak at 2175 cm^{-1}, it can be assumed that dimerisation in the compound occurs *mainly* through isopropoxy bridging as depicted below :



The presence of a shoulder at 2200 cm^{-1} indicates that further weak association (as depicted by observed average molecular complexity of 2.5) may be occurring through cyanide bridging.

The monocyano zirconium triisopropoxide shows only one absorption band at about 2160 cm^{-1} indicating the presence of only terminal cyano groups. The higher cyano derivatives of titanium and zirconium show mainly three absorption bands at about 2200±15, 2150±15 and 2060±20 cm^{-1} in the νCN stretching region. These three bands have been assigned [10-12] to the bridging cyanide, terminal cyanide and terminal isocyanide forms respectively. The appearance of bands of *increasing* intensity at about 2200±15 cm^{-1} shows that cyanide bridgings become more important as the cyano content in these derivatives increases.

Experimental

Stringent precautions were taken to exclude moisture. Benzene, cyclohexane, ethyl alcohol, isopropanol and acetone were dried by the usual techniques. Pyruvonitrile (Fluka) was used after distillation, b.p. 93°.

Alkoxides of titanium[13] and zirconium[14] were prepared by the standard ammonia method and purified by distillation and crystallization respectively.

Titanium and zirconium were estimated as their oxides and nitrogen was estimated by the Kjeldahl method.

Molecular weight determinations were carried out with a semi-micro Gallenkamp Ebulliometer with thermistor sensing in refluxing benzene and acetone.

Infrared spectra in the range 4000-400 cm^{-1} were recorded using a Perkin-Elmer model 337 Grating spectrophotometer.

Reaction of $Ti(OPr^i)_4$ with CH_3COCN in 1:1 molar ratio :

An exothermic reaction occurred when $Ti(OPr^i)_4$ (2.42 gm, 0.008 g mole) was treated with pyruvonitrile (0.59 gm, 0.008 g mole) in cyclohexane (~50 ml). The solution became yellow and turned black after some time. The reaction mixture was refluxed and the ester formed was removed azeotropically and the fractionation *was continued until* the boiling point of cyclohexane was reached. The reaction time was about 3 hrs. Excess of the solvent was *removed* under *reduced* pressure. A blackish, viscous compound, which fumes on exposure to atmospheric moisture was obtained.

The reactions between $Ti(OPr^i)_4$ and CH_3COCN in other stoichiometric ratios have been carried out similarly (Table 1).

The reactions between $Zr(OPr^i)_4.Pr^iOH$ and CH_3COCN have been carried out by first removing the coordinated isopropanol azeotropically and then adding CH_3COCN in different stoichiometric ratios and refluxing the reaction mixtures (Table 2).

TABLE 1—CYANIDE DERIVATIVES OF TITANIUM(IV) ALKOXIDES

S. No.	Reactants	(g.)	Molar Ratio	Yield in gms (Calcd.)	Product (Nature).	Analysis (%) Found (Calcd) Ti	Found (Calcd.) N	Mole-cular comp-lexity	IR assignment CN cm^{-1}
1.	$Ti(OPr^i)_4$ CH_3COCN	2.42 0.58	1:1	2.20 (2.14)	$Ti(OPr^i)_3(CN)$ black viscous)	18.90 (19.10)	5.44 (5.57)	2.5*	2200 sh, 2175 m
2.	$Ti(OPr^i)_4$ CH_3COCN	2.84 1.38	1:2	2.43 (2.68)	$Ti(OPr^i)_2(CN)_2.0.5X$ (black solid)	17.74 (17.83)	10.07 (10.40)	1.00**	2220 sh, 2170 m
3.	$Ti(OPr^i)_4$ CH_3COCN	2.06 1.93	1:3	2.50 (2.68)	$Ti(OPr^i)(CN)_3.X$ (black solid)	16.60 (16.69)	14.93 (14.63)	1.2**	2210 sh 2160 s, 2080 m
4.	$Ti(OPr^i)_4$ CH_3COCN	1.86 1.80	1:4	1.99 (1.99)	$Ti(CN)_4.1.5X$ (brown solid)	15.24 (15.71)	18.06 (18.36)	—	2200 m, 2150 m, 2075 w,
5.	$Ti(OEt)_4$ CH_3COCN	3.79 1.14	1:1	3.50 (3.46)	$Ti(OEt)_3(CN)$ (brown solid)	22.26 (22.92)	6.50 (6.69)	–	2160 w
6.	$Ti(OEt)_4$ CH_3COCN	3.46 4.18	1:4	4.36 (4.30)	$Ti(CN)_4.1.5\ Y$ (brown solid)	16.46 (16.87)	19.51 (19.71)	–	2050 s, 2000 – 1950 d
7.	$Ti(CN)_4.1.5X$ Pr^iOH	0.62	1:excess	0.40 (0.41)	$Ti(OPr^i)_2(CN)_2$ (brown solid)	22.20 (21.98)	12.35 (12.84)	—	

$X = CH_3COOPR^i$; $Y = CH_3COOEt$, * Mol. wt. in benzene ; ** Mol. wt. in acetone.

TABLE 2—REACTIONS OF ZIRCONIUM ISOPROPOXIDE ISOPROPONOLATE WITH PYRUVONITRILE

S. No.	Reactants	(gm)	Molar Ratio	Product (Nature)	Found (Calcd.) Zr.	Found (Calcd.) N	Assignments CN cm^{-1}
1.	$Zr(OPr^i)_4.Pr^iOH$ CH_3COCN	3.68 0.65	1:1	$Zr(OPr^i)_3(CN)$ (brown solid)	31.66 (30.99)	4.85 (4.75)	* 2160 w
2.	$Zr(OPr^i)_4.Pr^iOH$ CH_3COCN	2.92 1.04	1:2	$Zr(OPr^i)_2(CN)_2.0.5X$ (brown solid)	29.93 (29.21)	8.53 (8.96)	2200 m 2150 w, 2075 m 2050 w,
3.	$Zr(OPr^i)_4.Pr^iOH$ CH_3COCN	3.66 1.95	1:3	$Zr(OPr^i)(CN)_3.X$ (brown solid)	27.73 (27.61)	13.00 (12.71)	2200 w, 2150 w, 2080 w,
4.	$Zr(OPr^i)_4.Pr^iOH$ CH_3COCN	3.37 2.40	1:4	$Zr(CN)_4.2X$ (blackish brown solid)	23.02 (22.84)	14.32 (14.02)	2200 s, 2150 s, 2075 sh
5.	$Zr(OPr^i)_4.Pr^iOH$ CH_3COCN	1.70 0.31	1:1	$Zr(OPr^i)_3(CN).Pr^iOH$** (brown solid)	25.89 (25.74)	4.06 (3.95)	
6.	$Zr(OPr^i)_4.Pr^iOH$ CH_3COCN	1.75 1.26	1:4	$Zr(OPr^i)(CN)_3.X$** (brown solid)	27.31 (27.61)	12.83 (12.71)	
7.	$Zr(CN)_4.2X + Pr^iOH$	1.53 Excess	1:Excess	$Zr(OPr^i)_2(CN)_2.2Pr^iOH +$ $Zr(OPr^i)(CN)_3.2Pr^iOH$ (reddish solid)	25.16 (25.08)	9.36 (9.70)	

$X = CH_3COOPr^i$, * IR spectra in KBr pellet and other are in nuzol mull
** Reactions have been carried out at room temperature.

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ω-Bromoacetoacetanilide and Its Metal Chelates[a]

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Employing NMR technique, a bromo derivative of acetoacetanilide has been characterised to be ω-bromoacetoacetanilide. Infrared spectra of its metal chelates, $[BeL_2]$, $[CuL_2]$, $[VOL_2].4H_2O$, $[TiCl_2L_2]$ and $[UO_2L_2(H_2O)]$ (where L stands for ω-bromoacetoacetanilide in the enolate form) also support the same structure.

A number of investigators have studied bromination of acetoacetanilide[1-6]. Chudgar and Trivedi[7], however, proved conclusively that the product of bromination of acetoacetanilide in acetic acid medium is ω-bromoacetoacetanilide. To confirm the structure they also cyclised the compound to obtain 4-bromomethylcarbostyril. In view of our interest in metal chelates of the substituted acetoacetanilides, we have further characterised ω-bromoacetoacetanilide employing NMR technique and prepared its chelates with beryllium(II), a copper(II), titanium(IV) vanadium(IV) and uranium(VI).

Experimental

Preparation of ω-bromoacetoacetanilide:

ω-Bromoacetoacetanilide was prepared as reported[7].

Preparation of chelates:

Bis(ω-bromoacetoacetanilidato) copper(II): Dried metallic sodium chips (0.46g ; 0.02 mole) were added to a solution of ω-bromoacetoacetanilide (5g ; 0.02 mole) in cold methanol (150 ml). When the reaction subsided, the contents were warmed and a solution of copper(II) acetate hydrate (1.99 g ; 0.01 mole) in hot methanol (40 ml) was added while stirring. The complex which crystallised on cooling was filtered, washed successively with water and alcohol and recrystallised.

Oxobis(ω-bromoacetoacetanilidato) vanadium(IV): Prepared as above using a solution of oxovanadium(IV) sulphate pentahydrate (2.53 g ; 0.01 mole) in hot water (20 ml).

Dioxoaquabis (ω-bromoacetoacetanilidato) uranium (VI): An aqueous solution (100ml) of dioxouranium(VI) acetate dihydrate (4.24 g ; 0.01 mole) was added to an alcoholic solution (100 ml) of the bromoacetoacetanilide (5 g ; 0.02 mole) and stirred for 2 hr. The precipitated complex was filtered, washed with alcohol and recrystallised.

The chelates of beryllium(II) and titanium(IV) were prepared employing modified methods used for the syntheses of the corresponding acetoacetanilide chelates[8,9].

Infrared spectra of mulls in Nujol were recorded on a Perkin-Elmer 137 spectrometer. NMR spectrum was recorded on a Varian A 60 D spectrometer.

Results and Discussions

β-ketoamides exhibit keto-enol tautomerism in solution[10,11]. In DMSO-d_6, however, only four ^1H NMR signals were observed, showing that the enol form was negligible in the medium, for this simplified spectrum exclusively corresponds to that of the keto form. The signals are at 0.80 τ(singlet for -NH-), 2.80 τ(multiplet for $-C_6H_5$), 5.75 τ(singlet for $-CH_2Br$) and 6.20 τ(singlet for $-CH_2^-$). The integrated intensities correspond with the number of protons of each type.

Infrared spectrum of the compound shows two strong bands at 1725 and 1652 cm^{-1} for the bromoacetyl and the amide carbonyls respectively, In all its metal chelates (Table 1) these bands are shifted to about 1580 and 1600 cm^{-1} respectively (Table 2), showing[12] that both the oxygens of the ligand are bonded.

The broad N-H stretching band of the ligand around 3250 cm^{-1} is shifted upwards to ≃3320 cm^{-1} in the complexes. This shift indicates absence of nitrogen coordination[13,14].

Metal-ligand bonds in the complexes[9,14,15] are, therefore, depicted as in Figure 1.

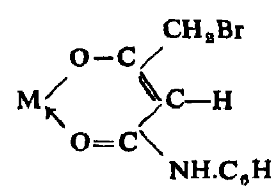


Fig. 1

All the metal chelates show a medium intensity band at 1195 cm^{-1}, assignable to >C-H in the plane bending vibration[8,16,17]. The presence of this band is an

(a) Presented at Convention of Chemists, 1976 (Ing. 13, p. 8 in Abstract).

TABLE 1—ANALYTICAL DATA AND OTHER DETAILS OF ω-BROMOACETOACETANILIDE AND ITS METAL CHELATES

Sl. no.	Compound	Solvent from which recrystallised	Yield (%)	Colour	m.p. (°C)	Analytical Data+ C (%)	H (%)	N (%)
1	ω-Bromoacetoacetanilide (LH)	Alcohol	80	Colourless	134	47.20 (46.88)	4.17 (3.90)	5.25 (5.47)
2	$[BeL_2]$	-do-	76	-do-	206-7	46.05 (46.24)	4.14 (3.85)	4.38 (5.38)
3	$[CuL_2]$	Acetone	60	Green	147	42.60 (41.84)	4.06 (3.48)	4.78 (4.89)
4	$[TiCl_2L_2]$	×	55	Reddish brown	**	(38.60 (38.16)	3.74 (3.18)	3.65 (4.45)
5	$[VOL_2]\text{-}4H_2O$	*	50	Greenish black	**	38.05 (37.56)	3.95 (4.06)	3.72 (4.38)
6	$[UO_2L_2(H_2O)]$	Acetone	73	Red	198-200d	31.25 (30.00)	3.26 (2.75)	2.94 (3.51)

+ Percentages found are noted first followed by calculated percentages in brackets. d. Decomposes.

** Not melting or visibly decomposing upto 360°

* Insoluble in common organic solvents, hence only washed repeatedly with warm solvents. × Though soluble in alcohol and methanol the complex decomposed in solution on standing. Hence only washed with cold and hot benzene.

TABLE 2—I. R. ABSORPTION FREQUENCIES (CM^{-1}) OF ETAL CHEMLATES OF ω-BROMOACETOACETANILIDE IN THE REGION 1750—1540 cm^{-1}.

Absorption[a] for chelates of Be	Cu	Ti	V	U	Assignments[8]
1603	1603	1603	1600	1603	Perturbed Amide I Frequency plus aromatic C.....C skeletal vibration frequency
1578	1580	1578	1578	1575	Perturbed carbonyl frequency plus another aromatic C.....C skeletal vibration frequency.
1554	1552	1553	1550	1540	Amide II frequency.

(a) All absorptions are strong.

evidence for the ligand molecule being ω-bromo- and not α-bromo-acetoacetanilide. Two strong bands at about 700 and 750 cm^{-1} (aromatic monosubstitution) are observed in the spectra of the ligand and its metal chelates.

β-Dicarbonyls react with titanium tetrachloride yielding complexes of the type prepared in this investigation[18,19,20]. Attempts to prepare $[TiCiL_3]$ from $[TiCl_2L_2]$ by refluxing with excess of the ligand[21], or by ligand exchange[9] were unsuccessful. This is probably due to the decreassed donor strength of the ligand resulting from bromine substitution.

The I. R. spectrum of the vanadyl complex shows a broad band in the 3650-3400 cm^{-1} region as may be expected for water of hydration[13]. Weak bands observed at about 3480 cm^{-1} in the I.R spectrum of the uranyl complex are attributed to coordinated water[22,24]. Similar aqua complexes of uranyl with β-diketone ligands have been reported[22-24].

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Salts of Metal Ions with Organic Arsonic Acids. Part VII. Salts of Nickel(II) with Arylarsonic Acids

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The polymeric salts of nickel(II) with phenylarsonic acid derivatives of 1:1 stoichiometry have been prepared and characterized by elemental analysis, magnetic susceptibility and IR and reflectance spectral data. Octahedral structure is proposed for all the salts except in case of *o*-nitrophenylarsonate where distorted tetrahedral structure is suggested.

THE study of arsonic acids and their salts is of theoretical as well as practical importance. These acids and their salts are being used as pesticides[1] to protect crops from pathological diseases, to treat chickens from protozoal infection[2] and to fight histomoniasis[3] and other diseases[4,5]. They have also been used as analytical reagents[6,7] in laboratory. Since transition metals are essential in plant nutrition[8], it was thought desirable to study the salts of arsonic acids with these metals.

Pietsch[9] studied the *p*H values at which the precipitation of nickel and other metal ions occurred with different arsonic acids. Basato and Peloso[10] studied the complexes of cobalt (II), nickel (II) and copper (II) with a Schiff base containing two arsonic acid groups. Salts of nickel (II) with methylarsonic acid[11], *o*-aminophenylarsonic acid[12,13] and phenylarsonic acid[13] have been reported.

In continuation of our studies on salts of phenylarsonic acids[13-19], salts of nickel(II) with arylarsonic acids have been isolated and their elemental analysis, magnetic susceptibilities at room temperature and IR and electronic spectra are being reported.

Experimental

Arylarsonic acids have been prepared by reported methods.[20,21] For obtaining a salt, alcoholic solutions of an arylarsonic acid (0.01 mole) and nickel acetate (0.01 mole, Riedel) were mixed and refluxed for about half an hour, when the green precipitate separated. The precipitate was filtered, washed repeatedly with hot alcohol and dried under vacuum.

Estimation of carbon, hydrogen and halogens was carried out by Australian Microanalytical Service, Melbourne. Nickel was estimated volumetrically using EDTA as a titrant.

The IR spectra of acids and salts were recorded as Nujol mulls on a Hilger and Watts H.800 Spectrophotometer (range 4000-650 cm^{-1}) using sodium chloride optics. The electronic reflectance spectra of salts were recorded on Unicam SP 700 A UV and Visible Spectrophotometer having SP 735 , diffuse reflectance attachment (range 50,000-4000 cm^{-1}).

The magnetic susceptibilities of the salts were measured at room temperature using Gouy method. The diamagnetic corrections were calculated on the basis of Pascal's constants.[22]

Results and Discussions

On the basis of elemental analysis (Table 1), the arylarsonates of nickel may be represented by the general formula, $X.C_6H_4AsO_3.Ni.\ n\ H_2O$, where n=O, 1/2, 1 or 3/2 and X=*p*-CH_3, *p*-Cl, p-Br, *p*-OCH_3, *o*-OCH_3 or *o*-COOH, except in the case of *o*-nitrophenyl arsonate, where the empirical formula is $O_2N.C_6H_4AsO_3.\ Ni.\ 1/2\text{-}C_2H_5OH$.

In the IR spectra of acids, ν(OH) occurs around 2750 and 2250 cm^{-1} [23], while in the spectra of salts, these bands are absent, indicating the bonding of both oxygens of $As\langle^{O}_{O}$ with nickel (II). This suggestion is further supported by the variation in the symmetric and asymmetric stretching frequencies[24] (Table 2) of $As\langle^{O}_{O}$ on salt formation. The ν(As=O) which occurs around 935-845 cm^{-1} *in arsonic acids, is shifted* by 20-100 cm^{-1} towards lower frequency in the salts of *p*-methyl-, *p*-chloro-, *p*-methoxy- and *o*-nitrophenylarsonic acids. A similar shift is observed in the salts of *p*-bromo-, *o*-methoxy- and *o*-carboxyphenylarsonic acids as well but the shifted bands are not clearly discernible as they overlap with the bands

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TABLE 1—ELEMENTAL ANALYSIS AND MAGNETIC SUSCEPTIBILITY DATA OF THE SALTS

Sr. No.	Salt	Calculated (%) C	H	X*	Ni	Found (%) C	H	X*	Ni	$\mu_{eff.}$ (B.M.)
1.	p-$CH_3.C_6H_4AsO_3Ni$	30.80	2.57	–	21.53	31.51	3.05	–	21.1	3.21
2.	p-$Cl.C_6H_4AsO_3Ni.H_2O$	23.13	1.93	11.4	18.87	23.67	2.03	11.5	18.5	3.07
3.	p-$Br.C_6H_4AsO_3Ni$	21.32	1.19	23.7	17.38	21.64	1.85	23.3	17.5	3.03
4.	p-$OCH_3.C_6H_4AsO_3Ni.H_2O$	27.39	2.93	–	19.12	27.94	3.04	–	18.9	3.25
5.	o-$OCH_3.C_6H_4AsO_3Ni.1/2H_2O$	28.28	2.69	–	19.72	28.73	3.56	–	19.6	3.20
6.	o-$COOH.C_6H_4AsO_3Ni.3/2H_2O$	25.48	2.43	–	17.80	25.81	3.42	–	18.0	3.33
7.	o-$NO_2.C_6H_4AsO_3Ni.1/2C_2H_5OH$	25.71	2,14	–	17.97	24.99	2.06	–	18.1	2.90

X* = Cl or Br

TABLE 2—INFRARED SPECTRAL DATA OF ARYLARSONIC ACIDS AND THEIR SALTS

Sr. No.	Acid	AsO_3 frequencies: As<(O)(O) Smym. stretch Acid	Salt	As<(O)(O) Asym. stretch Acid	Salt	As=O stretch Acid	Salt	As-C(aromatic) stretch Acid	Salt	Substituent group (in benzene ring) stretches Acid	Salt
1.	p-Methylphenylarsonic acid	765m	780m	785m	780m	845m, 865m	825m	1090s	1100s	–	–
2.	p-Chlorophenylarsonic acid	755m	735m	825m	780s	900m 915m	822s	1077s	1087s	1077s	1087s
3.	p-Bromophenylarsonic acid.	765m	780s	812m	820s	915m 935m	820s	1085w	1090w	1065m	1065s
4.	p-Methoxyphenylarsonic acid	755m	785mb	790m	785mb	890mb	825s	1095s	1100s	1015s 1257s	1025s 1250s
5.	o-Methoxyphenylarsonic acid	790m	765w	860w	810sb	910s	810sb	1125m	1125m	1010s 1235m	1015m 1255m
6.	o-Carboxyphenylarsonic acid	785m	745m	820w	835mb	855m	835mb	1085s	1115wb	1300s 1410w 3100wb 1637m 1650m	1305w 1410w 3100w 1550m 1600m
7.	o-Nitrophenylarsonic acid.	780m	780w	840w	805w	905s	870m	1105m	1095m	1330m 1515s	1330m 1515s

TABLE 3—ASSIGNMENTS OF ELECTRONIC SPECTRAL BANDS (CM^{-1}) AND CALCULATED VALUES OF LIGAND FIELD PARAMETERS (CM^{-1})

Sr. No.	Salt	$^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$	$^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$	$^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$	Dq	B
1.	p-$CH_3.C_6H_4AsO_3Ni$	8230	13510	23530	823	827
2.	p-$Cl.C_6H_4AsO_3Ni.H_2O$	8064	13330	23120	806	815
3.	p-$Br.C_6H_4AsO_3Ni$	8330	13790	23900	833	843
4.	p-$OCH_3.C_6H_4AsO_3Ni.H_2O$	8200	13330	23320	820	816
5.	o-$OCH_3.C_6H_4AsO_3Ni.1/2\ H_2O$	8200	13700	23650	820	841
6.	o-$COOH.C_6H_4AsO_3Ni.3/2\ H_2O$	8060	13990	23700	806	860
		$^3T_2(F) \leftarrow {}^3T_1(F)$	$^3A_2(F) \leftarrow {}^3T_1(F)$	$^3T_1(F) \leftarrow {}^3T_1(F)$		
7.	o-$NO_2\ C_6H_4AsO_3Ni.1/2\ C_2H_5OH$	4000	8400	13160	448	653

(835-810 cm^{-1}) due to As$<^{O}_{O}$ asymmetric stretch. This downward shift may be ascribed to tridentate nature of AsO_3 group in these salts.

The symmetric and asymmetric stretching frequencies of H_3C-O-$C_{aromatic}$ group appearing at 1010 and 1235 cm^{-1} respectively in o-methoxyphenylarsonic acid shift to 1015 and 1255 cm^{-1} respectively on the formation of a salt, indicating thereby the participation in bonding of -OCH_3 group with nickel(II).

In the spectrum of o-carboxyphenylarsonic acid the bands at 3100, 1410 and 1300 cm^{-1} may be assigned[26] to υ (OH), δ (OH) and ν (C-O) respectively. A doublet at 1650, 1637 cm^{-1} arises due to ν (C=O)[26]. Elemental analysis suggests that the proton of carboxylic acid group is not removed in salt formation. This is further supported by the presence of bands, though of weak intensities, at 3100, 1410 and 1305 cm^{-1} in the spectrum of the salt. However, the doublet at 1650, 1637 cm^{-1} of the acid shifts to 1610, 1550 cm^{-1} in the salt, indicating coordination of oxygen of C=O with nickel(II).

In p-bromo- and o-nitrophenylarsonates there is no change in the frequencies of substituted bromo and nitro groups. However, in the case of p-chloro- and p-methoxyphenylarsonates, a slight change in the position of bands of substituted groups is observed.

The results of magnetic susceptibility and electronic sepectral studies of the salts at room temperature are given in Tables 1 and 3 respectively. Except o-nitrophenylarsonate, all other salts of nickel(II) have magnetic moment in the range 3.11-3.35 BM. These values correspond to octahedral nickel(II) complexes[22]. The reflectance spectra confirm this conclusion. The assignment of various transtions to the observed bands are given in Table 3. Using the method of Lever[27], the values of Dq and B have been calculated. The ranges for the values of Dq and B in our salts are 806-833 cm^{-1} and 815-860 cm^{-1} respectively. These values almost correspond with the values of Dq=821 and B=875 cm^{-1} for octahedral phenylphosphonate of nickel, $C_6H_5PO_3Ni$, found by Grinonneau and coworkers[28]. Thus phenylphosphonic acid and arylarsonic acids have almost equal ligand field strength and nephelauxetic effect.

The reflectance spectrum of o-nitrophenylarsonate of nickel(II) differs from those of other salts. Where as in other salts the three observed bands are approximately at 8100, 13,700 and 23,700 cm^{-1}, in o-nitrophenylarsonate the bands are observed at 84.0, 13,200 and 31,250 cm^{-1}. The highest energy band has got high intensity, indicating it to be a charge transfer band. There are, therefore, only two ligand field bands in this salt. Absence of a ligand field band around 24,000 cm^{-1} and the magnetic moment value of 2.9 BM, which is characteristic of a distorted tetrahedral stereochemistry[22] for nickel(II), suggest that this salt does not have octahedral geometry. Assuming a tetrahedral stereochemistry of nickel(II) in this salts, the bands can be assigned to transitions as :

$$^3A_2\ (F) \leftarrow {}^3T_1\ (F),\ \nu_2 = 8400\ cm^{-1}$$

$$^3T_1^{\pi}\ (P) \leftarrow {}^3T_1\ (F),\ \nu_3 = 13,160\ cm^{-1}$$

The values of Dq = 448 cm^{-1} and B = 652 cm^{-1} are calculated on the basis of graphical method of Lever[27] for tetrahedral nickel(II) complexes. The band for the transition, $^3T_2(F) \leftarrow {}^3T_1(F)$, calculated on the basis of experimental values of ν_2 and ν_3 and calculated values of Dq and B should be at 3920 cm^{-1}. This band is found at 4000 cm^{-1} in the IR spectrum of the salt.

Thus the elemental analysis, magnetic data and electronic spectral study suggest a polymeric nature for these salts. This conclusion is substantiated by high melting points and insolubility of the salts in water and most of organic solvents.

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Potentiometric Study of Humic Acid Metal Interactions

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Potentiometric study of synthetic and natural humic acid (H. A.) fractions and their derivatives (nitro-, sulphonated and phosphorylated) in presence of heavy metal ions show the formation of ligand-metal complexes. The order and magnitude of *p*H -drop indicate the following order $Fe^{3+} > Al^{3+} > Cu^{2+} > Pb^{2+}$ in metal-ligand interactions. Of the various ligands, the complex formation capacity follows the order phosphorylated organic matter (o.m.) > nitrated o.m. > sulphonated o.m.

SOIL organic matter metal interactions play an important role in plant nutrition process, hence a study of such interactions is useful for prediction of the fate of a particular metal ion in soil.

All metal chelates may be considered as formed by the displacement of one or more weak acidic protons of the ligand by the metal ion, as a result, there is a drop in *p*H when chelate formation takes place. The greater the tendency of a metal ion to chelate with a particular organic ligand, the greater is the drop in *p*H (Martell and Chaberk[1]). Schnitzer and his co-workers[2] have shown that many metal ions undergo complexation with soil organic matter. Recently Adhikari and Hazra[3] have studied soil o.m. -metal interactions and are of opinion that hydroxylated type of metal-organic matter complexes are formed.

The object of the present paper is to investigate the interactions of different bi- and tri-valent metal ions with natural and synthetic H. A. fractions and their different derivatives viz. nitro, sulphonated and phosphorylated products.

Experimental

Natural H. A. is extracted from Kalimpong soil (0-15 cm depth), Darjeeling. The sodium carbonate extract is coagulated with HCl (*p*H 2.0) and different fractions are separated using standard procedure[4,13]. The H. A. is dialysed against distilled water and then electrodialysed. The fraction is then repeatedly resin treated and finally dialysed against H-resin (I.R.-12) to get H. A. hydrogen form.

Synthetic H. A. is prepared by the condensation of hydroquinone and glycine between *p*H 8.0 and 9.0 by refluxing in water bath for about 8 to 10 hours following the procedure of Coulson[5]. The contents are then precipitated with 1(M) HCl and H. A. fraction is separated by the usual procedure[4].

H. A. is sulphonated by BF_3/H_2SO_4 at 100° for about 90 minutes following the method of Mitsu[6]. It is nitrated by 15% HNO_3 with 5 times its weight of crude H. A. at 80° for two hours with constant shaking, and phosphorylated[8] with monosodium hydrogen phosphate at 100° under reduced pressure and then treated with water. The different derivatives are thoroughly dialysed. electrodialysed and repeatedly resin treated to get as their hydrogen form. The chemical analyses and average molecular weight of different o.m. are given in Table-1.

TABLE 1—ORGANIC MATTER

	Kalimpong soil (0-15 cm depth) Darjeeling Dt. West Bengal, India							
	H. A.	Nitro H.A.	Sulphonated H.A.	Phosphorylated H.A.	H.A.	Nitro H.A.	Sulphonated H.A.	Phosphorylated H.A.
Average mol. wt.	1020	850	1250	1860	2050	1680	2640	3260
%Carbon	48.2	48.18	45.32	44.45	52.31	47.51	49.45	48.31
%Hydrogen	5.18	6.22	3.15	3.20	7.02	9.02	6.02	5.95
%Nitrogen	1.95	3.14	2.01	2.02	5.05	6.12	3.86	3.52
%Sulphur	—	—	1.12	—	—	—	1.85	—
%Phosphorous	—	—		0.96	—	—	—	1.20

To a known amount of o.m. (o.m.=H. A. synthetic or natural, and their different derivatives), 2.0 ml of 0.01(N) NaCl are added and the volume is made upto 10.0 ml with distilled water. The sol is then titrated cautiously with standard NaOH solution and the corresponding *p*H of the sol is noted with a Cambridge *p*H meter at 30° equipped with a Cambridge glass electrode and a saturated calomel electrode with an aqueous agar-agar-KCl (saturated) salt bridge. In a similar way same amount of different o.m, in presence of metal salts (Fe^{3+}/Al^{3+}/Cu^{2+} as chloride and Pb^{2+} nitrate) required to form metal organic matter complexes are also titrated in a similar way by NaOH solution. Metal salt solutions are also titrated with NaOH. Mole ratios of o.m. metal ions used for preparation of the complexes are calculated from these potentiometric titration figures which are not shown here.

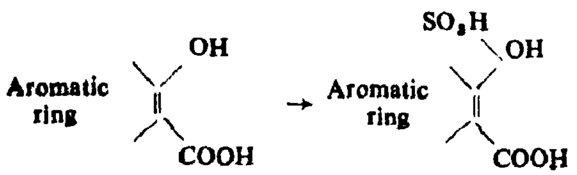
Different titration curves (not shown here) show the drop in *p*H (hence inflection in titration curves) and indicate the formation of metal-, ligand complexes[1,3]. The metal salt solutions are fairly acidic, initial drop in *p*H is not due to free metal ions, metal ions interact with the functional cites like CO-OH grs- OH grs of the ligands liberating protons for which the initial *p*H drop is observed. According to these earlier workers, greater the tendency of the metal ions to form chelates, the greater is *p*H drop and vary markedly with metal ions. The potentiometric titration, therefore, provides useful information regarding chelation reaction. However, there is a limitation in this study e.g. one should have a clear idea regarding molecular structure of the ligand (monodentate or bidentate) which is not known in the case because of the heterogeneity in structure. In spite of this, the study has its importance. Thus Fraser[15] from his study concluded that accumulation of toxic amounts of Cu in a forest peat was due to a sequence of events that included uptake of Cu from surrounding mineral soil by plant root, up ward translocation into leaf tissue in cooperation into humus layer of soil and transport to the swamp in seepage water as soluble organic complex. Coleman[9] observed that that Cu^{2+} displaced the titration curves of acid washed peat and stated as due to the complex formation which were corroborated by others. According to them the formation of water soluble hydroxylated complexes in H. A. metal interactions is the cause of *p*H drop.

In this study the magnitude of *p*H drop upon addition of different metal ions follows the order $Fe^{3+} > Al^{3+} > Cu^{2+} > Pb^{2+}$, which is in accordance with the results of earlier workers[12]. In the present study it is noted that sulphonated and nitrated H. A. possess lower tendencies to combine with a given metal ion than that of the original o.m., on the other hand phosphorylation markedly increased the chelate forming tendency of the o.m. It is, however, known[10] that nitro- and sulphonic acid groups are electron acceptors and if they are linked directly to benzene ring, the acidity of the phenolic hydroxyl group increases and the basicity of $-NH_2$ group decreases. Due to this coordinating tendencies of these groups are lowered. Hence it appears that these groups have taken their positions in the aromatic core of H. A. and thus have effects on the coordinating groups. On phosphorylation, in addition to the already present groups, phosphorus enters into complex formation with metal ions. The stability of the complexes thus increases. In order to get an idea about the mechanism of these reactions between o.m. and metal ions, number of protons released by NaOH during the titration of o.m. and mixture of o.m. and metal ions are calculated and reported in Tables 2 and 3.

TABLE 2—PROTONS RELEASED PER MOLE OF ORGANIC MATTER (H.A.)

*p*H	Kalimpong H.A.	Kalimpong Sulpho-H.A.	Kalimpong Nitro-H.A.	Kalimpong Phospho-H.A.	Synthetic H.A.	Synthetic Sulpho-H A.	Synthetic Nitro-H.A.	Synthetic Phospho-H.A.
4.0	—	1.84	—	—	—	—	—	—
4.5	—	2.76	—	—	0.87	0.40	0.56	—
5.0	1.65	3.5	1.38	0.95	2.18	1.8	1.7	—
5.5	2.83	4.6	2.48	2.2	3.65	4.0	2.3	0.50
6.0	3.67	6.44	3.2	2.4	4.9	6.4	3.4	1.00
6.5	4.75	7.3	4.00	2.8	5.6	8.0	4.5	1.4
7.0	5.41	9.6	4.60	3.2	6.4	8.6	5.1	1.6
7.5	5.80	11.96	5.0	3.5	7.3	9.4	5.6	1.9
8.0	6.16	—	5.5	3.96	8.2	10.2	6.2	2.2
8.5	6.9	—	6.3	4.8	9.4	12	—	2.8
9.0	8.0	—	7.7	—	—	—	—	3.96

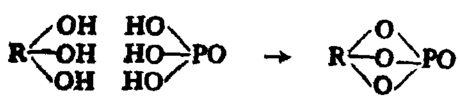
From Table 2 it is evident that at pH 5.5, approximately three COOH groups, at pH 7.5 and at pH 8.0 six -COOH groups are neutralised for Kalimpong H. A. At pH 9.0 in addition to six-COOH groups two phenolic hydroxyl groups are also neutralised. On sulphonation greater number of protons are released per mole of o.m. at any particular pH, in comparison to those released from H. A. alone. But on nitration and phosphorylation number of protons released per mole of o.m. decreases. This probably is due to the fact that on sulphonation, additional number of acid sulphonic groups are introduced in the H. A. molecule. Sulphuric acid behaves both as an oxidising as well as a sulphonating agent. Perhaps due to the oxidising character of the acid, the phenolic and to some extent the -COOH groups have been oxidised and $-SO_3H$ groups have taken their places in the aromatic core of humic acid molecules or it may so happen that sulphuric acid may enter the vacant positions in benzene ring. If this happens, then the acidic properties of humic acid will show an increase in value in the way :



But on nitration, because of the oxidising property of HNO_3, some breakdown of H. O. A. structure (as appeared in decrease in average mol. wt.) might have occurred causing a decrease in carboxylic groups. On phosphorylation, phenolic hydroxyl groups are blocked by phosphoryl groups, possibly some change in the structure of H. A. might have taken place. It appears that simple reaction of phosphoric acid by the phenolic hydroxyl group would show an increase in acidic property of the phosphorylated product as

$$\text{Ph-OH} + \text{HO-PO/OH/OH} \quad \text{Ph--OP--O/OH/OH} \downarrow \text{Ph-O-PO}_3^{2-} + 2H^+$$

But, no such effect noticed in this case and hence such simple reaction does not take place. Due to the complex structure of humic acids, a number of phenolic-OH groups simultaneously interact with the phosphoric acid, the resultant effect will be the decrease in acidity of the product.



R = aromatic core of humic acid

Similar observations are noted in titrating synthetic H. A. and its different derivatives, namely sulphonated, nitrated and phosphorylated products as shown in Table 2.

The difference of protons set free from different o.m. metal complexes can be explained by writing the following simplified equations as suggested earlier[2,3,14]

(a) When no metal ions are added—

$R(COOH)_6 + 6NaOH = R(COONa)_6 + 6H_2O$ – six protons are released

R = H. A. without six – COOH groups

$R(COOH)_{4-5} + (4-5)NaOH = R(COONa)_{4-5} + (4-5)H_2O$ – four to five protons are set free

R = Nitro H.A. without four to five – COOH groups.

$R(SO_3H)_4(COOH)_5 + 9NaOH = R(SO_3Na)_4(COONa)_5 + 9H_2O$ – nine protons are released

R = H. A. without four – SO_3H and five – COOH groups.

When M^{2+} salt is added—

(b) $R(COOH)_6 + MCl_2 + 6NaOH = R(COONa)_4(COO)_2M + 2NaCl + 6H_2O$ – six protons are set free

(c) $R(COOH)_6 + MCl_2 + 7NaOH = R(COONa)_5(COO)M(OH) + 6H_2O + 2NaCl$ – seven protons are set free

(d) $R(COOH)_6 + MCl_2 + 8NaOH = R(COONa)_6 + M(OH)_2 + 2NaCl + 6H_2O$ – eight protons are set free

When M^{3+} salt is added—

(e) $R(COOH)_6 + MCl_3 + 6NaOH = R(COONa)_3M + 3NaCl + 6H_2O$ – six protons are set free

(f) $R(COOH)_6 + MCl_3 + 7NaOH = R(COONa)_4(COO)_2M(OH) + 3NaCl + 6H_2O$ – seven protons are set free

(g) $R(COOH)_6 + MCl_3 + 8NaOh = R(COONa)_5(COO)M(OH)_2 + 3NaCl + 6H_2O$ – eight protons are set free

(h) $R(COOH)_6 + MCl_3 + 9NaOH = R(COONa)_6 + M(OH)_3 + 3NaCl + 6H_2O$ – nine protons are set free

Similar types of reactions with metal ions and nitrohumic acid most probably take place. Reactions of metal ions with sulphonated H. A. may proceed in the following way :

(i) with bi-valent metal ions :

(a) $R(SO_3H)_4(COOH)_5 + MCl_2 + 10NaOH = R(SO_3Na)_4(COOH)_4(COO)M(OH) + 2NaCl + 9H_2O$ – ten protons are set free

or

(b) $R(SO_3H)_4(COOH)_5 + MCl_2 + 10NaOH = R(SO_3Na)_3(COONa)_5(SO_3)M(OH) + 2NaCl + 9H_2O$ – ten protons are set free

(ii) with tri-valent metal ions :

(a) $R(SO_3H)_4(COOH)_6 + MCl_3 + 11NaOH =$
$R(SO_3Na)_4(COO)M(OH)_2$ $3NaCl + 9H_2O$ – eleven protons are set free

(b) $R(SO_3H)_4(COOH)_6 + MCl_3 - 11NaOH =$
$R(SO_3Na)_3(COONa)_6(SO_3)M(OH)_2 + 3NaCl + 9H_2O$ – elevent protons are set free.

The number of protons released from the sulfonated product by titration with NaOH may be explained by these probale reactions. This does not bear any relation to the moleculr weight of the complexes. Reactions bi- or tri-valent metal ions with phosphorylated derivative could not be depicted as above because how the phosphoryl groups enter into reactions with different metal ions could not be definitely ascertained from the present study.

TABLE 3—PROTONS RELEASED PER MOLE OF METAL ADDED FROM

	Kalimpong H.A. by				Kalimpong Sulpho H.A. by				Kalimpong Nitro-H.A. by				Kalimpong Phospho-H.A. by			
*p*H	Pb^{2+}	Cu^{2+}	Al^{3+}	Fe^{3+}	Pb^{2+}	Cu^{2+}	Al^{3+}	Fe^{3+}	Pb^{2+}	Cu^{2+}	Al^{3+}	Fe^{3+}	Pb^{2+}	Cu^{2+}	Al^{3+}	Fe^{3+}
4.5	—	—	—	—	—	0.99	1.40	1.46	—	—	—	—	—	—	—	—
5.0	0.48	0.80	1.80	2.00	0.66	1.21	1.90	1.95	0.80	1.00	1.80	1.60	0.56	0.33	1.54	2.57
5.5	−0.52	0.96	1.80	1.88	0.88	1.54	2.30	2.68	0.92	1.08	1.80	1.60	0.46	0.26	1.43	1.95
6.0	−1.50	0.96	1.98	1.90	1.23	1.54	2.40	1.59	1.90	1.60	2.00	1.60	0.67	0.56	1.87	1.95
6.5	−1.48	0.90	1.73	2.00	2.2	1.76	2.60	2.01	—	1.50	2.50	1.74	0.96	0.81	2.31	1.951.11
7.0	−1.70	1.12	2.34	2.90	—	—	2.90	3.17	—	1.50	2.62	1.81	1.11	0.91	2.64	2.1
7.5	—	1.60	3.24	—	—	—	—	—	—	1.80	2.82	2.00	1.11	0.32	3.24	—
8.0	—	2.24	—	—	—	—	—	—	—	2.00	—	2.61	—	1.58	—	—

	Synthetic H.A. from				Sulpho Synthetic H.A. from				Nitrated Synthetic H.A. from				Phospho Synthetic H.A. from			
*p*H	Pb^{2+}	Cu^{2+}	Al^{3+}	Fe^{3+}	Pb^{2+}	Cu^{2+}	Al^{3+}	Fe^{3+}	Pb^{2+}	Cu^{2+}	Al^{3+}	Fe^{3+}	Pb^{2+}	Cu^{2+}	Al^{3+}	Fe^{3+}
4.5	—	0.88	1.73	1.60	—	0.80	1.40	1.85	—	0.91	1.41	1.69	—	—	—	—
5.0	1.05	1.18	1.83	1.70	0.80	1.20	2.20	2.59	0.63	1.08	1.80	1.90	—	—	—	—
5.5	1.17	1.03	1.83	1.50	1.0	2.00	2.80	—	0.72	0.92	2.20	2.38	0.43	0.84	1.74	1.93
6.0	1.40	1.18	1.83	1.44	2.2	2.30	3.00	—	0.72	1.08	2.40	2.85	0.37	0.94	1.99	2.17
6.5	1.30	1.18	2.40	1.70	—	2.32	3.00	—	1.44	1.08	2.60	—	0.37	0.98	2.03	2.32
7.0	1.30	1.03	—	1.93	—	2.00	—	—	1.80	1.26	2.90	—	0.64	1.03	2.13	2.60
7.5	—	1.18	—	2.5	—	2.22	—	—	—	1.44	—	—	0.74	1.05	2.26	2.72
8.0	—	—	—	—	—	—	—	—	—	1.44	—	—	0.80	1.05	2.46	2.83
8.5	—	—	—	—	—	—	—	—	—	—	—	—	0.96	2.17	—	2.83

On comparison of data in Table 3 with the above reactions it may be said that the complex formation between natural H. A. and synthetic H. A. with divilent metal ions proceeds according to the equation (c) between *p*H 4.5 to 7.0 for natural H. A. and between *p*H 4.5. to 7.5 for synthetic preparations, since approximately one proton is released per mole of metal added within this *p*H range. In this *p*H- range Cu^{2+} is present as $Cu(OH)^+$ and Pb^{2+} which form electrovalent bonds with negatively charged carboxyl groups. The results corroborate the earlier findings of Khanna and Stevenson[11]. It is also observed that upto *p*H 7.0 for natural H. A. and upto *p*H 7.5 for synthetic preparation, the complexes with Pb^{2+} and Cu^{2+} are stable. Above this *p*H these complexes break down releasing approximately two protons per mole of metal added according to the equation (d).

TABLE 4—PROTONS RELEASED PER MOLE OF METAL ION FROM

*p*H	Pb^{2+}	Cu^{2+}	Al^{3+}	Fe^{3+}
4.0	1.69	—	—	0.76
4.5	1.95	—	—	1.52
5.0	2.08	—	1.4	2.83
5.5	2.20	0.47	1.84	3
6.0	—	1.01	2.21	—
6.5	—	1.66	2.53	—
7.0	—	1.92	2.90	—

Reactions of bi-valent metal ions with sulphonated and nitrohumic acids (both natural and synthetic preparations) appear to be similar in nature except that for sulphonated product the complex breaks above *p*H 5.0 (both for Kalimpong sulpho H. A. and synthetic preparations). However, with nitro- H. A. the complex is stable upto *p*H 5.5 for natural product and upto *p*H 7.0 for synthetic nitro-H. A. In case of phosphorylated H. A. (both natural and synthetic preparations) it is observed that the complex with Cu^{2+} is highly stable upto *p*H 8.0 above which it however breaks up, with Pb^{2+} the complex is stable upto *p*H 7.0.

The situation with trivalent metal ions may be explained as follows :

Natural o.m. reacts with Al^{3+} according to the equation (g) where Al^{3+} is present as $Al(OH)_2^+$ and between *p*H 5.0 to 7.0 approx. 2.0 protons are released per mole of metal. Reaction of Al^{3+} with synthetic o.m. occurs according the equation (f) where Al^{3+} is present as $Al(OH)^{2+}$ and between *p*H 4.5 to 6.0 approx. 1.0 to 1.5 protons are thus released per mole of metal. Above *p*H 6.0 and upto *p*H 7.0 Al^{3+} is probably present as $Al(OH)_2^+$ as approx. 2.0 protons are released per mole of metal and the reaction seems to proceed according to the equation (g). Reaction with Fe^{3+} seems to be similar to that for Al^{3+} where approximately 2.0 protons are released per mole of Fe^{3+} within the *p*H range 4.5 to 7.0 when Fe^{3+} is present as $Fe(OH)_2^+$. For sulphonated and nitrated products although similar types of reactions occur but the complexes break down at lower *p*H. Comparatively nitro-product are more complexing agent than sulphonated products. Trivalent metal ions from stable complexes with phosphorylated o.m. and the complexes are stable upto higher *p*H range e.g. for Fe^{3+} complex upto *p*H 7.0 for natural derivative and upto *p*H 8.0 for synthetic derivative.

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Chromatographic Separations on Anion-Exchange Papers

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A comparative study of the chromatographic behaviour of anions phosphate, vanadate, chromate, molybdate and tungstate on anion-exchange papers and Whatman no. 1. filter papers using identical aqueous-organic mixed solvent system has been made. The selectivity of separation increases greatly in the case of anion exchange papers in which the separation is sharp and the spots are distinct in contrast to Whatman no. 1. filter papers where wide and diffused bands are obtained. Methyl alcohol, ethyl alcohol, n-butyl alcohol, iso-amyl alcohol in combination with acetone, hydrochloric acid or acetic acid of different molarity have been used as the developing solvent. The anions phosphate, vanadate, chromate, molybdate, tungstate are separated from each other when they are present in a binary or in a complex mixture. The method is applied to analyse an alloy steel.

THE importance of inorganic ion-exchangers for the separation of metal ions has been increased during the last ten years. Among different inorganic ion exchangers, hydrated stannic oxide acts as an anion exchanger at $pH<6.0$[1] and as a cation-exchanger at $pH>6.0$[1-3].

Combined ion-exchange and solvent extraction (C.I.E.S.E.) technique has been utilised by several authors as a useful tool for the separation of different metal ions in mixture using usual synthetic organic ion exchange papers[4-12]. A few works with C.I.E.S.E. technique have been reported so far using inorganic ion exchangers[13] and systematic studies on the development of C.I.E.S.E. technique for the separation of anions are still lacking.

In this paper are reported the results of systematic studies using inorganic anion exchanger, hydrated stannic oxide, impregnated papers and mixed aqueous organic solvent system. The anions phosphate, vanadate, chromate, molybdate, tungstate are separated from each other when they are present in a binary or in a complex mixture. The aqueous organic solvent system studied are: The ternary mixtures of methanol, ethanol, n-butanol or isoamyl alcohol as one of the components and acetone and hydrochloric acid or 20% acetic acid as the other two components. A comparative study has also been made with ordinary Whatman No. 1. filter papers using identical solvent compositions.

Experimental

Apparatus and Reagents

Developments were carried out in (30×7cm) glass jars using the ascending method on (25×3 cm) paper strips. Sodium stannate was of reagent grade quality (U.S.S.R.). All other chemicals and solvents used were either of B.D.H. or E. Merck analar grade. The anion solution used for separation contained one mg. of each salt per ml. of the solution. Sodium or potassium or ammonium salts were used.

Preparation of hydrated stannic oxide papers

Each paper strip was dipped in freshly prepared 1(*M*) aqueous solution of sodium stannate for 10 seconds. It was then removed and kept horizontally at (30±5)° in air oven for 30 minutes. Dried papers were then dipped in 1 (*M*) aqueous solution of ammonium sulphate for 10 seconds and dried horizontally at first at (30±5)° for two hours and then at (85±5)° for one hour. The dried papers were washed several times with double distilled water and dried at room temperature.

In order to check the conversion of sodium stannate into hydrated stannic oxide via ammonium stannate, 25 ml. of 1(*M*) sodium stannate solution was taken and tin was estimated iodimetrically[14]. Again, 25 ml of 1(*M*) sodium stannate solution was taken and was mixed with 25 ml. of 1(*M*) ammonium sulphate solution.

* Senior Author. Part of this paper was presented at the symposium on "Recent Trends in Ion-exchange" at Roorkee on 20.12.75.

The white precipitate of hydrated tin dioxide was filtered, washed with distilled water and dried at 85° for one hour and weighed to constant weight.

TABLE NO. 1—CONVERSION OF SODIUM STANNATE INTO HYDRATED SnO_2

No. of obs.	Volume of 1(M) $Na_2SnO_3 \cdot 3H_2O$ solution taken each time (ml.)	Amount of SnO_2 obtained iodimetrically (g)	Amount of SnO_2 obtained at 85°C. (g)	Amount of SnO_2 obtained at 800°C (g)
1.	25	3.545	3.951	3.521
2.	25	3.543	3.952	3.523
3.	25	3.544	3.956	3.525

It is evident from the above data (Table-1) that the conversion of sodium stannate into tin dioxide via ammonium stannate under the condition is almost quantitative.

In order to determine the composition of the impregnated paper, ten numbers of each of the plain Whatman No. 1. papers and hydrated stannic oxide impregnated papers were ignited at 850° and weighed to constant weight. The average amount of SnO_2 obtained per sheet of Whatman papers is 315.70 mg. and the amount of SnO_2 per square centimetre is 4.20 mg.

It was experimentally observed that hydrated stannic oxide prepared from sodium stannate by precipitation and dried at (80±5°) for one hour as above was chemically stable in the solvent systems used in the chromatographic separation.

Spraying Reagents

Usual spraying reagents were used for the detection of different ions.

General procedure

Paper strips were lightly marked with pencil line to indicate the starting and finishing position of the solvent fronts and the starting position of the ions to be separated. The mixture of anions was then spotted on the pencil line and allowed to come in contact with solvent mixture in each case by ascending paper chromatography. Care had been taken to keep the diameter of the spot within 5 mm. The development of the spots were then carried out with the spraying reagent. The R_T and R_L values were then measured atleast for triplicate runs and their average were noted. A series of chromatographic runs were also made using the identical solvent system on hydrated stannic oxide loaded papers and ordinary Whatman No. 1 papers.

Results and Discussion

The R_T and R_L values for the anions in different solvent systems are given in Tables 2 to 6.

TABLE NO. 2—R_T, R_L AND R_F VALUES OF PHOSPHATE AND MOLYBDATE ON HYDRATED STANNIC OXIDE PAPER AND WHATMAN—1 PAPER AT (30±2)°C.

Time—One hour

Solvent system	(R_T-R_L) R_F value on hydrated stannic oxide paper	(R_T-R_L) R_F value on Whatman-1 paper
HCl(6*M*)-acetone -CH_3OH = 3:1·1 (vol/vol.)	molybdate (0.58-0.75)0.66 phosphate (0.15-0.32)0.23	phosphate (0.89-1.00)0.94 molybdate (0.63-0.86)0.74
HCl(6*M*)-acetone -C_2H_5OH = 3:1:1 (vol/vol)	molybdate (0.58-0.67)0.62 phosphate (0.05-0.14)0.05	phosphate (0.84-1.00)0.92 molybdate (0.60-0.7)0.65
HCl(6*M*)-acetone -n-butanol = 3:1:1 (vol/vol)	molybdate (0.48-0.66)0.57 phosphate (0.00-0.00)0.00	phosphate (0.86-1.00)0.93 molybdate (0.69-0.77)0.73
HCl(6*M*)-acetone -isoamylalcohol = 3:1:1 (vol/vol)	molybdate (0.64-0.80)0.72 phosphate (0.20-0.34)0.27	phosphate (0.84-1.00)0.92 molybdate (0.50-0.72)0.61

TABLE NO. 3.—R_T AND R_L VALUES OF CHROMATE AND PHOSPHATE, CHROMATE AND VANADATE, CHROMATE AND MOLYBDATE ON HYDRATED STANNIC OXIDE PAPER AND WHATMAN-1 PAPER AT (30±2)°C.

Time—One hour

Solvent system		(R_T-R_L) value on hydrated stannic oxide paper	(R_T-R_L) value on Whatman-1 paper
HCl(2*M*)-acetone-n-butanol=3:1:1 (vol/vol).	(a)	Chromate (0.72-0.80) Phosphate (0.00-0.00)	Chromate (0.77-0.96) Phosphate (0.77-0.96)
	(b)	Chromate (0.72-0.78) Vanadate (0.24-0.31)	Chromate (0.77-0.96) Vanadate (0.77-0.96)
	(c)	Chromate (0.73-0.78) Molybdate (0.00-0.04)	Chromate (0.70-0.96) molybdate (0.70-0.96)

TABLE NO. 4—SELECTIVE SEPARATION OF TUNGSTATE FROM THE SYNTHETIC MIXTURE OF TUNGSTATE, PHOSPHATE, MOLYBDATE AND VANADATE.

Temperature=(30±2)°C Time—One hour.

Solvent system	(R_T-R_L) value on hydrated stannic oxide paper	(R_T-R_L) value on Whatman-1 paper
20% CH_3COOH-acetone-C_2H_5OH =2:1:2 (vol/vol)	tungstate (0.82-0 92) phosphate (0.00-0.00) molybdate (0.00-0.00) vanadate (0.00-0.00)	*tungstate (0.82-0.94) *phosphate (0.72-0.84) molybdate (0.29-0.45) vanadate (0.12-0.20)

* Note :—With Whatman—1 paper overlapping of tungstate and phosphate took place.

TABLE NO. 5—R_T AND R_L VALUES OF TUNGSTATE, CHROMATE AND VANADATE ; TUNGSTATE, CHROMATE AND PHOSPHATE ; TUNGSTATE, CHROMATE AND MOLYBDATE ON HYDRATED STANNIC OXIDE PAPER AND WHATMAN-1 PAPER AT (30±2)°C.

Time—One hour

Solvent system		(R_T-R_L) value on hydrated stannic oxide paper	(R_T-R_L) value on Whatman-1 paper
20% CH_3COOH-acetone-C_2H_5OH=2.5 :1:1.5 (vol/vol)	(a)	tungstate (0.88-0.98) chromate (0.25-0.37) vanadate (0.00-0.00)	*tungstate (0.87-0.94) *chromate (0.69-0.89) vanadate (0.05-0.22)
	(b)	tungstate (0.90-0.98) chromate (0.25-0.39) phosphate (0.00-0.00)	*tungstate (0.87-0.94) *chromate (0.69-0.89) *phosphate (0.66-0.70)
	(c)	tungstate (0.88-0.98) chromate (0.26-0.37) molybdate (0.00-0.00)	*tungstate (0.87-0.94) *chromate (0.69-0.89) molybdate (0.16-0.46)

* Note :—With Whatman No. 1 paper, in all the cases overlapping of tungstate and chromate, in some cases overlapping of chromate and phosphate took place.

TABLE NO. 6—SEPARATION OF CHROMATE, MOLYBDATE, VANADATE AND PHOSPHATE FROM EACH OTHER IN A MIXTURE.

Temperature=(30±2)°C Time—One hour

Solvent system	(R_T-R_L) value on hydrated stannic oxide paper	(R_T-R_L) value on Whatman-1 paper
HCl(2M)-acetone-C_2H_5OH=3:1:1 (vol/vol)	Chromate (0.67-0.75) molybdate (0.20-0.27) vanadate (0.05-0.11) phosphate (0.00-0.00)	*Chromate (0.87-0.98) *molybdate (0.65-0.78) *vanadate (0.80-0.91) *phosphate (0.78-0.90)

* Note :—With Whatman-1 paper overlapping of all four ions took place.

In the case of binary mixture of phosphate and molybdate (Table-2) poor separation and in some cases no separation at all were observed with ordinary Whatman No. 1 papers, whereas the separation was sharp and spots were distinct in hydrated stannic oxide loaded papers, using same time and exactly identical conditions. With Whatman No. 1 papers diffused and wide spots were observed. Another remarkable observation was that in the case of ordinary paper phosphate occupied higher position than molybdate, but with hydrated stannic oxide loaded paper the case was reversed. That was either due to strong adsorption of phosphate on hydrated stannic oxide or due to the formation of insoluble stannic phosphate. In the presence of 6(*M*) hydrochloric acid and small amount of molybdate the probability of the formation of phosphomolybdic acid was negligible. Molybdenum moved on the paper most probably as the species MoO_2Cl_2. At 6(*M*) hydrochloric acid the species was weakly absorbed by anion exchanger. When the acidity of hydrochloric acid decreased to 2(*M*) molybdate did not move and was adsorbed strongly by the exchanger (Table-3).

It was also observed that the difference of R_F values of the anions calculated from R_T and R_L values (Table-2) increased with the increase of molecular weight of the primary alcohols. The difference of R_F values increased in the order $CH_3OH < C_2H_5OH <$ n-butyle alcohol, but the difference of R_F values for isoamyl alcohol were intermediate between that of CH_3OH and C_2H_5OH.

It was also observed that with hydrated stannic oxide loaded paper the R_F values for phosphate and molybdate were maximum for isoamyl alcohol but with primary alcohols the R_F values for both decreased with the increase of molecular weight. This order of decreasing R_F values with increasing molecular weight of the primary alcohols was not so regular with ordinary Whatman No. 1 papers.

In the case of tungstate and vanadate, tungstate and phosphate, tungstate and molybdate it was found that almost in all Whatman no. 1 papers tungstate was widely distributed throughout the paper and no distinct and clear cut spot was observed. In many cases there were overlapping of the two and separations were not possible. But with hydrated stannic oxide loaded papers the tungstate was well separated from others and sharp well defined spots were obtained. From the R_T and R_L values of tungstate, phosphate, molybdate and vanadate it was quite clear that tungstate could be selectively separated from the mixture of phosphate, vanadate and molybdate. This selective separation of tungstate was obtained from the synthetic mixture of phosphate, vanadate, molybdate and tungstate (Table-4).

In the case of chromate and vanadate, chromate and phosphate, chromate and molybdate (Table-3) overlapping took place with Whatman No. 1 papers and no separation was possible, whereas with hydrated stannic oxide loaded papers chromate was separated from phosphate, vanadate and molybdate from its binary mixtue. From the study of the R_T and R_L values of chromate, vanadate, phosphate and molybdate it was found that with hydrated stannic oxide loaded paper chromate could be selectively separated from the mixture of vanadate, phosphate and molybdate. A synthetic mixture of phosphate, chromate, vanadate and molybdate was used and a clear cut separation was obtained. [Table No, 6, Fig. 1, b]. The difference of R_T and R_L values of different ions indicated that ethyl alcohol-acetone-hydrochloric acid 2(*M*) and n-butanol-acetone-hydrochloric acid 2(*M*) were the best medium. Since n-butanol is immiscible with 2(*M*) hydrochloric acid, it is difficult to study the separation at different proportions of the solvent mixture. This difficulty did not arise with ethyl alcohol-acetone-hydrochloric acid 2(*M*) system. This developing solvent mixture was, therefore, the best solvent for all such separations.

In the case of ternary separation of tungstate, chromate and vanadate, tungstate, chromate and phosphate and tungstate, chromate and molybdate (Table-5) it was observed that no separation was possible with Whatman No. 1 paper, but clear cut separation was achieved with hydrated stannic oxide loaded papers.

Application to an alloy steel (*BAS no. 64A*)

200 mg. of the steel was taken and solution was made by usual procedure[14]. Total volume of the solution was made 100 ml. so that 1 ml. of the solution contained 2 mg. of the alloy steel. The solution was tested for chromate, tungstate, vanadate and molybdate, and positive results were obtained[15]. As in the previous cases the alloy solution was spotted on the papers and allowed to come in contact with the developing solution of 20% acetic acid-acetone-ethyl alcohol (2 : 1 : 2 vol/vol) for one hour. After drying the papers were first sprayed with (1:1) hydrochloric acid and then warmed. Tungstate and vanadate produced yellow colour. Then chromate was detected by diphenyl carbazide and molybdate by hydrogen sulphide. Good separation was observed [Table-7,]. It was noted that due to presence of mineral acid in the alloy steel solution vanadate was eluted and moved a little upward on hydrated stannic oxide papers.

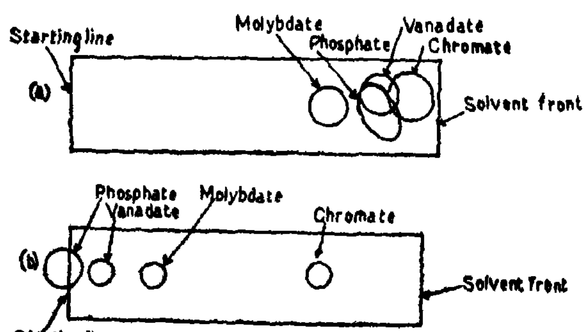


Fig. 1. Separation of the anions on : (a) Whatman no 1 filter paper (b) Hydrated stannic oxide loaded paper

TABLE NO. 7—ANALYSIS OF AN ALLOY STEEL (BAS NO. 64a)

Temperature=(35±1)°C — Time—One hour

Solvent system	(R_T-R_L) value on hydrated stannic oxide paper	(R_T-R_L) vaule on Whatman-1 paper
20% CH_3COOH-acetone-C_2H_5OH =2:1:2 (vol/vol)	tungstate (0.85-0.96) chromate (0.47-0.57) vanadate (0.13-0.20) molybdate (0.00-0.00)	*tungstate (0.82-0.98) *chromate (0.75-0.98) vanadate (0.09-0.18) molybdate (0,30-0.40)

*Note :—With Whatman-1 paper overlapping of tungstate and chromate took place.

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Dibromamine-T as an Analytical Reagent : Estimation of Thiosemicarbazide and its Metal Complexes

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A simple, rapid and accurate method for the estimation of thiosemicarbazide and its metal complexes with Zn, Cd, Hg, Co, Ni and Pd in aqueous or *p*H 4 buffer medium by a direct titration with dibromamine-T (DBT) in presence of sodium acetate and KBr has been developed. A back titration procedure in which TSC and its complexes (including those of Pt) in aqueous or *p*H 4 buffer medium are oxidised by DBT has also been described. The oxidation involves a twelve electron stoichiometry per TSC molecule in both direct and back titration procedures. The proposed analytical methods are useful for a rapid estimation of TSC and its complexes on a macroscale and also for computing the number of ligand molecules in a TSC metal complex.

THE number of suitable oxidants available in non-aqueous redox titrimetry are limited. Nair *et al* have introduced the organic haloamines, dichloramine-T (DCT)[1] and dibromamine-T (DBT)[2] as redox titrants in non-aqueous media. The former has been extensively used in our laboratories,[3,4] to determine a variety of reductants. Recently, Nair and Indrasenan[2] have employed DBT to determine Sb(III), As(III), Tl(I), Fe(II) and compounds such as ferrocyanide, iodide, ascorbic acid, hydroquinone, hydrazine, aniline, phenol and oxine. The present studies extend their investigations of DBT for estimating thiosemicarbazide and its metal complexes. Thiosemicarbazide (TSC) and its derivatives are well known metal complexing agents. They have a number of applications such as in characterization of aldehydes, ketones and polysaccharides. They are antitubercular, active against influenza, protozoa, smallpox and certain kinds of tumour and are possible pesticides and fungicides, due to their ability to chelate trace metals. The methods for the estimation of TSC reported so far are based on its oxidation by alkali metal hypohalites,[5,6] chloramine-T,[4,7] dichloramine-T[4] and lead tetraacetate,[8]. We have now critically examined the behaviour of DBT towards TSC and its metal complexes. It was found that TSC in the pure state as well as in its complexes is oxidized by DBT with a twelve electron change per molecule under specified conditions. After careful investigations, rapid and accurate analytical techniques have been proposed for estimating TSC and its complexe with zinc group of metals and cobalt, nickel, platinum and palladium, by DBT. The proposed volumetric methods for their estimation include (i) a direct titration between the reductants and DBT in presence of KBr and sodium acetate, with a visual or potentiometric end point and (ii) a back titration procedure in presence of sodium acetate.

Materials and Methods

E. Merck thiosemicarbazide was purified by recrystallisation from aqueous solution. $PdCl_2$ and $H_2PtCl_6 \cdot xH_2O$ (Johnson-Matthey Ltd., London) were used for preparing the Pt(II) and Pd(II) complexes. The following TSC(L) complexes were prepared by methods reported by us elsewhere :[8-10] ML_2X_2, where M = Zn, Cd, Ni or Hg ; X = Cl, NO_3, ClO_4 or $\frac{1}{2}SO_4$; $CoL_3(NO_3)_3$; cis and trans PtL_2Cl_2, PtL_2X_2 where X=Br, I, CN, CNS or NO_3; cis and trans-$PdL_2(NO_3)_2$; PdL_2X_2 where X=Cl, Br, I or CNS; Neutral complexes $M(L-H)_2$ where M = Ni, Pt or Pd. Solution of TSC and its complexes were prepared in aqueous medium or in *p*H 4 acetate buffer (~2 mgl/ml). Approximately 1NKBr 20% sodium acetate, and 10% zinc sulphate solutions were prepared. Triply distilled water was used for preparing the solutions. DBT was prepared and purified by the method of Nair and Indrasenan[2]. An approximately decinormal solution in glacial acetic acid was prepared, standardised by the iodometric method and stored in amber coloured bottles. All other materials and reagents were of accepted grades of purity. A Bajaj potentiometer with a platinum indicator electrode and a reference calomel electrode was used for potentiometric titrations.

1. *Direct titration :*

(a) *With visual end point* : A direct titration of TSC and its complexes (with the exception of those of Pt) with DBT was found practicable in the presence of sodium acetate and KBr, the former to accelerate the decomposition of DBT and the latter to serve as an indicator to detect the end point in an Andrews type of titration, employing carbon tetrachloride. The presence of a small quantity of $ZnSO_4$ solution was necessary in the titration of pure TSC with DBT.

Recommended procedure ; Take aliquots of TSC or its complex (~2-60 mg) in a 100 ml iodine flask. Add 5 ml of sodium acetate and 5 ml of KBr and 1 ml of CCl_4 (5 ml of $ZnSO_4$ solution in case of pure TSC) and titrate with DBT with shaking till the appearance of a faint yellow colour in CCl_4 layer (Appearance of

faint yellow colour in the aqueous layer indicates the approach of end point in the absence of CCl_4). Blank correction was found to be about 0.05 ml of 0.1*N* DBT. The amount (x mg) of TSC or its complex in the sample solution is given by $x=\frac{M}{E}$ NV, where N is the normality of DBT, V, the volume of DBT required, M is the molecular weight of TSC or its complex and E is the number of electrons changing per molecule of TSC or its complex.

(b) *Potentiometric end point :* A potentiometric titration of TSC and its complexes with DBT was possible in presence of sodium acetate (5 ml) and KBr (5 ml). A large potential jump of ~200 – 400 mV was noticed for the addition of 0.1 ml of 0.1*N* oxidant at the equivalence point. In the absence of sodium acetate, premature end points were obtained. Addition of a small quantity of $ZnSO_4$ (5 ml) was essential in the titration of pure TSC with DBT.

Platinum complexes of TSC could not be titrated directly with DBT, since their oxidation was non-stoichiometric under these conditions.

2. *Back titration method :*

Preliminary investigations : In preliminary investigations known quantities of TSC or its complex solution were added to a known excessive volume of DBT in an iodine flask. The reaction mixture was set aside for various intervals of time at room temperature with occasional shaking. The excess of DBT left unconsumed was iodometrically determined by back titration with standard sodium thiosulphate.

It was found that with a 40 – 50% excess of DBT, the oxidation of TSC was completed in 20 minutes, if an over-all water content of about 10 – 20% was maintained in the reaction mixture. Stoichiometric oxidation of complexes of Zn, Cd, Hg, Ni and Co took

TABLE 1 – ESTIMATION OF THIOSEMICARBAZIDE AND ITS METAL COMPLEXES WITH DIBROMAMINE-T (DIRECT TITRATION)

Compound	Range studied (mg)				
	Taken	Visual end point		Potentiometric end point	
		Found	Deviation %	Found	Deviation %
TSC(L)	2.07-62.10	2.08-61.73	0.10-0.60	2.08-61.75	0.10-0.56
ZnL_2SO_4	2.11-52.77	2.12-52.70	0.10-0.47	2.12-52.70	0.13-0.52
ZnL_2Cl_2	2.09-52.35	2.09-52.27	0.00-0.41	2.09-52.09	0.00-0.41
$ZnL_2(NO_3)_2$	2.05-51.15	2.04-51.27	0.23-0.59	2.04-51.27	0.23-0.59
$ZnL_2(ClO_4)_2$	2.08-52.08	2.09-51.80	0.27-0.54	2.07-51.80	0.10-0.54
CdL_2SO_4	2.03-50.62	2.03-50.50	0.00-0.42	2.03-50.60	0.00-0.44
CdL_2Cl_2	2.06-51.50	2.07-51.30	0.10-0.51	2.05-51.36	0.10-0.49
HgL_2Cl_2	2.03-50.69	2.04-50.61	0.02-0.49	2.04-50.61	0.13-0.49
PdL_2Cl_2	1.34-33.59	1.34-33.47	0.00-0.60	1.35-33.47	0.11-0.75
PdL_2Br_2	1.70-29.74	1.69-29.68	0.00-0.59	1.70-29.68	0.00-0.52
PdL_2I_2	2.40-30.00	2.41-30.06	0 20-0.50	2.41-30.06	0.00-0.50
$PdL_2(CNS)_2$	1.36-30.51	1.37-30.56	0.16-0.74	1.37-30.36	0.25-0.74
cis-$PdL_2(NO_3)_2$	1.32-39.47	1.32-39.40	0.00-0.66	1.31-39.40	0.18-0.76
trans-$PdL_2(NO_3)_2$	2.64-39.59	2.64-39.66	0.00-0.48	2.63-39.66	0.08-0.76
$Pd(L\text{-}H)_2$	1.79-44.79	1.80-44.60	0.11-0.56	1.79-44.85	0.00-0.48
$CoL_2(NO_3)_2$	2.30-57.39	2.30-57.16	0.00-0.44	2.31-57.16	0.26-0.68
$NiL_2SO_4.3H_2O$	2.11-52.88	2.12-52.61	0.19-0.52	2.10-52.63	0.09-0.47
$NiL_2(NO_3)_2$	2.11-52.79	2.11-52-57	0.00-0.54	2.10-52.73	0.00-0.51
NiL_2Cl_2	1.88-56.28	1.87-56.19	0.16-0.53	1.89-56.11	0.09-0.53
$Ni(L\text{-}H)_2$	2.04-50.90	2.05-50.66	0.03-0.49	2.04-50.84	0.00-0.59

TABLE 2 — ESTIMATION OF THIOSEMICARBAZIDE AND ITS METAL COMPLEXES WITH DIBROMAMINE-T (BACK TITRATION)

Compound	Range studied (mg) Taken	Found	% Deviation
TSC(L)	2.07-62.10	2.08-61.75	0.10-0.56
ZnL_2SO_4	2.11-52.77	2.12-52.70	0.03-0.52
ZnL_2Cl_2	2.09-52.35	2.09-52.08	0.00-0.52
$ZnL_2(NO_3)_2$	4.09-51.15	4.11-51.14	0.00-0.49
$ZnL_2(ClO_4)_2$	2.08-52.08	2.09-52.15	0.13-0.48
CdL_2SO_4	2.03-50.62	2.03-50.74	0.00-0.42
CdL_2Cl_2	2.06-51.50	2.07-51.53	0.06-0.49
HgL_2Cl_2	2.03-50.69	2.02-50.83	0.02-0.49
PdL_2Cl_2	1.34-33.59	1.33-33.47	0.15-0.75
PdL_2Br_2	1.70-29.74	1.71-29.68	0.20-0.71
PdL_2I_2	1.20-30.00	1.20-29.93	0.00-0.50
$PdL_2(CNS)_2$	1.36-30.51	1.35-30.36	0.13-0.74
cis-$PdL_2(NO_2)_2$	2.63-39.47	2.62-39.40	0.20-0.61
trans-$PdL_2(NO_2)_2$	1.32-39.59	1.32-39.66	0.00-0.48
$Pd(L\text{-}H)_2$	1.79-44.79	1.80-44.60	0.11-0.56
$CoL_3(NO_3)_3$	2.30-57.39	2.29-57.09	0.19-0.52
$NiL_2SO_4.3H_2O$	2.11-52.88	2.10-52.63	0.09-0.47
$NiL_2(NO_3)_2$	2.11-52.79	2.11-52.68	0.00-0.41
NiL_2Cl_2	1.88-56.28	1.89-56.11	0.00-0.53
$Ni(L\text{-}H)_2$	2.04-50.90	2.04-50.66	0.00-0.59
cis-PtL_2Cl_2	2.11-52.85	2.12-52.63	0.13-0.61
trans-PtL_2Cl_2	1.06-31.86	1.06-31.91	0.00-0.56
PtL_2Br_2	1.78-31.15	1.79-31.22	0.09-0.56
PtL_2I_2	2.54-38.10	2.55-37.99	0.16-0.55
$PtL_2(CN)_2$	1.02-30.65	1.02-30.53	0.00-0.52
$PtL_2(CNS)_2$	2.21-33.18	2.21-33.13	0.00-0.54
$PtL_2(NO_2)_2$	1.35-40.46	1.35-40.58	0.00-0.55
$Pt(L\text{-}H)_2$	2.75-41.34	2.75-41.47	0.00-0.58

place within 5 – 10 minutes. Pd and Pt complexes could be oxidised within 10 – 15 and 30 – 40 minutes respectively. The rate was very slow with TSC solutions in glacial acetic acid.

Recommended procedure : Add aliquots of TSC or its complex solution to a known excessive volume of 0.1*N* DBT (~40 – 50% excess) in an iodine flask (5 ml $ZnSO_4$ solution in the case of pure TSC) maintaining an over-all water content of about 10 – 20%. Shake the contents and set aside for the duration mentioned above. Add 10 ml of 20% potassium iodide solution and titrate with 0.1*N* sodium thiosulphate (V_1). Run a blank with DBT solution (V_2). The amount of TSC or its complex (x mg) in the sample solution is given by $x = \frac{M}{E}N(V_2 - V_1)$, where N is the normality of thiosulphate and E and M have the significance as before.

Results and Discussion

The ligand TSC in the pure state and in its metal complexes is oxidized with a-12 electron change under both direct and back titration procedures. It was noticed that the CN^- and CNS^- present in $PtL_2(CN)_2$, $PtL_2(CNS)_2$ and $PdL_2(CNS)_2$ are also oxidised by the oxidant under these conditions with a 2 and 8-electron change per ion respectively. Allowance was made for this fact in calculating the amount of complex recovered. With cobalt complex liberation of one equivalent of iodine by Co^{3+} has been excluded, in recovery calculations.

The stoichiometry of oxidation of TSC in the pure state and in its complexes can be represented as follows :

$$NH_2NHCSNH_2 + 3\ RNBr_2 + 6\ H_2O \longrightarrow$$

$$3\ RNH_2 + CO_2 + H_2SO_4 + N_2 + NH_4Br + 5HBr \quad ...(1)$$

$$M(NH_2NHCSNH_2)_2X_2 + 6\ RNBr_2 + 12\ H_2O \rightarrow$$

$$MX_2 + 6\ RNH_2 + 2\ CO_2 + 2\ N_2 + 2\ H_2SO_4 + 10\ HBr + 2\ NH_4Br \quad ...... (2)$$

where M = Zn, Ni, Cd, Hg, Pt or Pd and X = Cl, NO_3, ClO_4, Br, I or $\frac{1}{2}$ SO_4

$$M(NH_2NCSNH_2)_2 + 6\ RNBr_2 + 12\ H_2O \longrightarrow$$

$$MSO_4 + 6\ RNH_2 + 2\ CO_2 + 2\ N_2 + 10\ HBr + 2\ NH_4Br + H_2SO_4 \quad ... (3)$$

where M = Ni, Pt or Pd, $R = p - CH_3 - C_6H_4SO_2$.

Similar equations can be written for $PtL_2(CN)_2$, $PtL_2(CNS)_2$, $PdL_2(CNS)_2$ and $CoL_3(NO_3)_3$.

Some typical results of analyses are shown in tables 1 and 2. The tables show the range of amounts of TSC and its complexes employed and recovered and the per cent error in the recovery. Each range covers the amounts present in 8 – 10 different aliquots of the compound, It is seen that the results are accurate with an error of about 0.5%.

Common anions such as SO_4^{2-}, PO_4^{3-}, NO_3^-, ClO_4^-, Cl^- and F^- do not interfere but I^- ion interferes in direct titration and Br^- ion in the back titration. N_2H_4 interferes in both the titrations. It was found that presence of water and alkali acetate accelerates the rate of oxidation.

It can be concluded from the above investigations that the proposed analytical techniques are rapid and accurate and are useful for estimating macroquantities of the ligand in the pure state and in its complexes by a proper adjustment of reaction conditions. Also an

approximate computation of the number of ligand molecules present in a TSC complex can be made by these analytical techniques.

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Titrimetric Determination of Antimony(V) with Iron(II)

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A direct titrimetric method has been developed for the determination of antimony(V) using iron(II) as a reductimetric reagent in a strong phosphoric acid medium. The phosphoric acid concentration should be at least 11*M* (70% V/V) and hydrochloric acid concentration 2*M* for a satisfactory titration. The end point can be determined either potentiometrically or using thionine as indicator. Sulphate, perchlorate and acetate ions do not interfere in this method ; arsenic(V), copper(II), selenium(IV), selenium(VI) and tellurium(VI) interfere. Tellurium(IV) does not interfere upto an overall concentration of 0.004*M*. The formal redox potentials of the Sb(V)/Sb(III) couple in media of varying phosphoric acid concentration have been determined for the first time.

EARLIER methods[1-4] for the determination of antimony(V) consist in treating antimony(V) with excess of KI in acid medium and titrating the liberated iodine with hypo. In these methods a coloured compound of the formula $SbCl_3 . 3KI.5H_2O$ which is sometimes formed was stated to seriously interfere with the titration. In a few other methods antimony(V) is reduced in acid solution either with KI[5] or with iodine solution and red phosphorous[6], the liberated iodine boiled off with excess of carbon dioxide and the antimony(III) formed titrated with standard iodine solution. McCay[7] determined antimony(V) by shaking $3-4N$ HCl solutions in a mercury reductor in an atmosphere of carbon dioxide for one hour and titrating the antimony(III) formed with $KBrO_3$ using methyl orange as indicator. Schreider[8] accomplished the reduction of antimony(V) with SO_2 and the antimony(III) formed was determined by the bromate method after boiling off the excess SO_2. Tananaev and Davitashvili[9] determined antimony(V) by treating it with tin and HCl and titrating the tin(II) formed in the reaction with $KMnO_4$. In the more recent methods the determination of antimony(V) is carried out potentiometrically by titrating with tin(II)[10], vanadium(III)[11], chromium(II), vanadium(II), titanium(III), and thiourea[12].

Eventhough a large number of methods are available for the titrimetric determination of antimony(V), no method is entirely satisfactory, because the visual end point methods are tedious while the potentiometric ones need an inert atmosphere, high temperatures and special apparatus for the storage of the reductant solutions. We have now developed a titrimetric method for the determination of antimony(V) using iron(II) as a reductimetric reagent in a strong phosphoric acid medium, which does not suffer from the disadvantages mentioned above. The end point can be determined at room temperature either potentiometrically or using thionine as indicator.

Experimental

Solutions : An approximately 0.025*M* solution of antimony(V) was prepared by dissolving about 3 gms. of sodium pyroantimonate (BDH, LR) in 250 ml of concentrated hydrochloric acid and making it upto 500 ml. Its strength was determined employing the method of McCay[7].

Approximately 0.025*M* solution of antimony(III) was prepared by dissolving about 0.36 gms of antimonous oxide (May & Baker, LR) in 50 ml of concentrated hydrochloric acid and making it upto 100 ml. Its strength was determined with potassium bromate using methyl red as indicator.

Approximately 0.05*M* solution of iron(II) was prepared from ferrous ammonium sulphate (BDH. Analar) and standardised in the usual way.

A 0.1% solution of thionine was prepared in water. Basynth, A. R., phosphoric and hydrochloric acids were used in this investigation. The strengths of these acids were determined with standard solutions of sodium hydroxide using "Elico" p^H meter Model 10.

Apparatus : OSAW potentiometer and suspension galvanometer were used. A bright platinum electrode (0.2 mm diameter) was used as the indicator electrode and a saturated calomel electrode as the reference electrode. An agar-agar salt bridge containing 30% of potassium chloride was used.

Procedure : To an aliquot volume (upto 10 ml) of antimony(V) solution taken in a 150 ml beaker, 70 ml of phosphoric acid and enough hydrochloric acid to give an overall concentration of 2*M* were added. The solution was titrated with iron(II) solution while it was being stirred by means of a magnetic stirrer. The

potentials were measured 30 seconds after the addition of each instalment of the titrant till 75% of the titration was completed. There afterwards stable potentials were obtained only after waiting for two minutes after the addition of the titrant. However, at the end point one has to wait for four minutes for the stable potentials to be established. After the equivalence point the potentials get stabilised immediately after the addition of iron(II). The break in potential at the end point corresponds to about 60mV/0.04 ml of 0.05*M* iron(II).

The titration can also be carried out using a visual indicator. The conditions for the visual titration were the same as for the potentiometric one except that three drops of thionine should be added and a carbon dioxide atmosphere maintained to prevent aerial oxidation of the leuco base of the dye. The colour change at the end point is from green to pale yellow.

Results and Discussion

Some of the representative results obtained using the procedures described above are shown in Table 1.

TABLE 1—TITRIMETRIC DETERMINATION OF ANTIMONY(V) WITH IRON(II)

Potentiometric method Antimony(V), mg.		Visual end-point method Antimony(V), mg.	
Taken	Found	Taken	Found
9.14	9.17	7.56	7.53
13.98	14.02	10.47	10.50
15.50	15.45	13.31	13.37
20.28	20.20	15.50	15.45
23.72	23.67	18.88	18.94
29.05	29.02	29.90	29.90

The accuracy of the potentiometric method was ±0.4% and that of the visual indicator method was ±0.5%. The precision in both the methods was determined by titrating ten samples each containing 15.50 mg of antimony(V). The averages and standard deviations were 15.502 mg and 0.04 mg in the potentiometric method and 15.504 mg and 0.05 mg in the visual indicator method.

During the reduction of antimony(V) with iron(II) in phosphoric acid medium it was noticed that the reduction proceeds quantitatively to antimony(III) provided the medium contains at least 11*M* (or 70% by volume) phosphoric acid and 2*M* hydrochloric acid. In order to explain the conditions necessary for the quantitative reduction of antimony(V), a knowledge of the formal redox potentials of Sb(V)/Sb(III) couple and Fe(III)/Fe(II) couple in media of varying phosphoric acid concentration is necessary. The data on the redox potentials of the Fe(III)/Fe(II) couple in varying phosphoric acid concentrations were avilable from the work of Gopala Rao and Sagi[13]. However, the formal redox potentials of Sb(V)/Sb(III) couple in media of varying phosphoric acid concentrations were not available from the literature. We have, therefore, determined the formal redox potentials of Sb(V)/Sb(III) couple in media of varying phosphoric acid concentrations, adopting a method essentially similar to that described by Gopala Rao and Dikshitulu[14] for the determination of the formal redox potentials of V(IV)/V(III) couple in phosphoric acid medium. The potentials were determined at 30° keeping the total [antimony] at 0.0025*M* and the total dilution at 100 ml. In addition to phosphoric acid the solutions contain 0.5*M* hydrochloric acid. The potential data thus obtained are tabulated in Table 2.

TABLE 2—FORMAL REDOX POTENTIALS OF Sb(V)/Sb(III) COUPLE IN MEDIA OF VARYING PHOSPHORIC ACID CONCENTRATIONS

Concentration of Phosphoric acid, M	Formal redox potential (N.H.E.), V
3.0	0.872
4.0	0.848
6.0	0.808
8.0	0.776
10.0	0.752
12.0	0.744
14.0	0.740

These potentials are reproducible within ±5mV. The potential data incorporated in Table 2 along with that of the Fe(III)/Fe(II) couple is shown graphically in Fig. 1. The potential data could not be determined accurately below 3*M* phosphoric acid concentration because of the hydrolysis of antimony solutions.

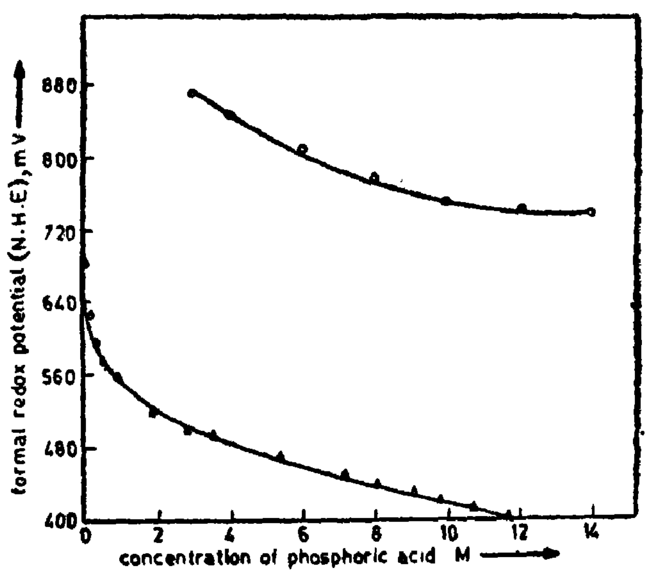


Fig. 1. Formal Redox Potential of Sb^{V}/Sb^{III} (⊙—⊙) and Fe^{III}/Fe^{II} (Δ—Δ) couples in a medium of varying phosphoric acid concentration.

From Fig. 1. it may be seen that the potentials of both Sb(V)/Sb(III) and Fe(III)/Fe(II) couples decrease with increasing phosphoric acid concentration. However, it appears surprising that even though the potential difference between the two couples at various phosphoric acid concentrations is nearly equal, the reduction proceeds quantitatively only at a phosphoric acid concentration of 11*M* or above. Thus the potentials data does not seem to be helpful in explaining the conditions needed for the quantitative reduction of antimony(V) to antimony(III).

For a rapid and quantitative reduction of antimony(V) to antimony(III), in addition to a minimum concentration of about 11*M* phosphoric acid, a chloride ion concentration of 2*M* was found to be necessary. The authors feel that chloride ion facilitates the electron transfer from iron(II) to antimony(V) probably through the formation of a bridged complex. Bromide ion was found to catalyse the reaction better than the chloride ion, thus strengthening our contention that these ions facilitate the reaction through the formation of a halide bridge. However, even bromide ion should be present at a concentration of more than 1*M* for the titration to be satisfactory. Since it is difficult to provide such a high concentration of bromide ion (excepting through the use of hydrobromic acid which is not a common reagent in the laboratory) we preferred the use of chloride ion in the titration.

Interferences

Among the anions sulphate, perchlorate and acetate ions do not interfere ; arsenic(V) interferes by slowly getting reduced to arsenic(III). Among the cations, copper(II), selenium(IV), selenium(VI) and tellurium(VI) interfere. Tellurium(IV) does not interfere upto an overall concentration of 0.004*M*.

Acknowledgement

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Solvent Extraction and Spectrophotometric Determination of Rhenium(VII) using Mixed Ligands

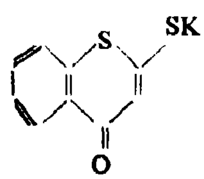
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A new method is proposed for the extraction and spectrophotometric determination of rhenium(VII) using 2-mercaptobenzo-γ-thiopyrone (MBTP) and ammonium thiocyanate as mixed ligands. The colour formation is complete in 30 min. and the complex is stable for over 24 hr at room temperature. The complex is formed in 1.8-2.6 *N* HCl medium and is extracted into acetophenone, giving an absorbance maximum at 435 nm. The method is more sensitive than any of the other spectrophotometric methods reported for rhenium. Many commonly associated ions do not interfere; while serious interferences from Mo^{6+}, W^{6+}, U^{6+}, V^{5+}, Se^{4+}, Ni^{2+}, and Cu^{2+} are eliminated by a chloroform-tertiary amine extraction prior to the determination of rhenium. An improved method for the separation of molybdenum(VI) before the determination of rhenium is also developed. Three substituted derivatives of MBTP have also been tried as mixed ligands with ammonium thiocyanate.

IN a previous communication[1] we have shown that the sensitivity of the colour reaction for the solvent extraction and spectrophotometric determination of rhenium with thiocyanate in presence of stannous chloride can be considerably increased if a mixture of thiocyanate and thiourea are used. In the present work we have observed that the sensitivity of the rhenium reaction can be further increased if a mixture of thiocyanate and potassium salt of 2-mercaptobenzo-γ-thiopyrone, MBTP, (i) are used as mixed ligands.



2-mercaptobenzo-γ-thiopyrone (i)

Based on this colour reaction, an efficient and sensitive spectrophotometric method is developed which is described in this paper.

5-hydroxy-8-nitro(ii), 7-hydroxy-8-nitro-(iii) and 5-hydroxy-6, 8-dinitro(iv) derivatives of MBTP were also prepared and employed as mixed ligands with thiocyanate to find out their applicability.

Experimental

The reagent MBTP was prepared by refluxing acetophenone, carbon disulphide and alcoholic potassium hydroxide[3]; the derivatives of MBTP were prepared in a similar way using 3-nitro-6-hydroxy acetophenone[4], 3-nitro-4-hydroxy acetophenone[5] and 3, 5-dinitro-6-hydroxy acetophenone[6] in place of acetophenone. The solid obtained in each case was filtered and washed with ether. Recrystallisation from a 1:1 chloroform-ether mixture gave pale yellow crystals for MBTP and yellow, yellowish green and yellowish brown crystals for the derivatives respectively. Analysis: (i) Found 27.52% S and 16.80% K; calcd. for $C_9H_5OS_2K$, 27.57% S and 16.[illegible]5% K. (ii) Found 21.80% S, 13.42% K and 4.84% N; calcd. for $C_9H_4O_4NS_2K$, 21.84% S, 13.35% K and 4.78% N. (iii) Found 21.92% S, 13.40% K and 4.85% N; calcd. for $C_9H_4O_4NS_2K$, 21.84% S, 13.35% K and 4.78% N. (iv) Found 18.85% S, 11.62% K and 8.32% N; calcd. for $C_9H_3O_6N_2S_2K$, 18.93% S, 11.57% K and 8.28% N.

Aqueous solution of 5% (W/V) ammonium thiocyanate and 1% (W/V) MBTP were used as mixed ligands reagent.

Stannous chloride solution was prepared by dissolving 11.5 g $SnCl_2 \cdot 2H_2O$ in 17 ml conc. HCl with dilution to 100 ml with distilled water.

Potassium perrhenate was obtained from Johnson Matthey and Co. Ltd., London, and was used without further purification. A standard solution of rhenium was prepared by dissolving 10 mg of potassium perrhenate in distilled water and making up the volume to 100 ml. The rhenium content per ml was determined spectrophotometrically using thiocyanate-stannous chloride method[2].

Acetophenone (BDH) used for extraction was purified by distillation.

All other reagents used were of AnalaR quality.

Apparatus

Absorbances were measured with a Beckmann DU2 spectrophotometer with 1 cm quartz cells.

Procedure

Place an aliquot of the rhenium solution containing 3 to 40 μg of the metal in a separatory funnel and add 1 ml of 10 *M* HCl followed by 2 ml of 5% (W/V) ammonium thiocyanate, 1 ml of 1% (W/V) MBTP and 1 ml of stannous chloride solution. Shake gently for 1 min. and set aside for 30 min. for colour to develop. Then extract the colour with 3 ml of acetophenone and draw out the solvent layer into a small beaker containing 1 g anhydrous sodium sulphate. Repeat the extraction twice more with 2 ml portions of acetophenone and collect in the same beaker. Transfer the combined extract to a 10 ml volumetric flask and make up the volume with the solvent. Measure the absorbance at 435 nm against the reagent blank.

Results and Discussion

The absorbance spectra of rhenium thiocyanate, rhenium-MBTP and the mixed ligand complexes are shown in Fig 1. The absorbance of the mixed ligand complex increases from 375 nm, passes through a maximum at 435 nm and then decreases, whereas the absorbance of the reagent blank decreases from 375 nm upto 440 nm and then slightly increases. For spectrophotometric measurements 435 nm was chosen as the optimum wavelength.

Maximum colour intensity was obtained in 1.8 to 2.6 *N* hydrochloric acid. Sulphuric acid and nitric acid were found unsuitable, because the former produced a turbidity while the latter reduced the colour intensity.

Absorbance remained constant from 1.7 to 3.1 ml of 5% (W/V) ammonium thiocyanate, 0.9 to 2.5 ml of 1% (W/V) MBTP and 0.9 to 1.4 ml of stannous chloride. However, 2 ml of thiocyanate, 1 ml of stannous chloride were used for experimental purposes.

The order of addition of ligands to rhenium solution containing hydrochloric acid had no effect on absorbance, but stannous chloride should be added only at the end.

Variation of temperature between 150° and 50° had no effect on colour formation. The complex was stable for over 24 hr at room temperature.

Optimum range, sensitivity and photometric error

The colour system obeyed Beer's law from 0.3 to 4.2 ppm of rhenium at 435 nm and the optimum concentration range determined by the method of Ringbom[7] was 0.5 to 3 ppm. In this range the percentage relative analytical error per 1% absolute photometric error[8] was 2.9. The photometric sensitivity of the method was 0.003 μg Re/Cm^2 at 435 nm.

The absorbance spectra of mixed ligand complexes of rhenium with thiocyanate and the three derivatives of MBTP are shown in Fig 2 with those of the respective

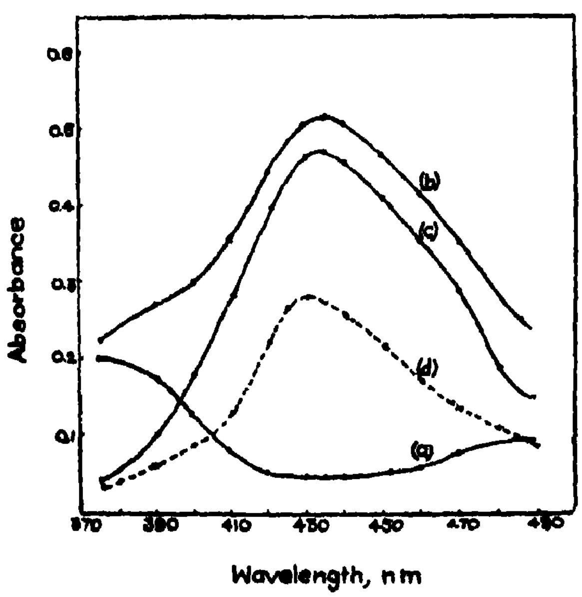


Fig. 1. Absorption spectra

a) Reagent (1 ml 10 *M* HCl, 2 ml 5% (W/V) ammonium thiocyanate, 1 ml 1% (W/V) MBTP and 1 ml stannous chloride) vs. acetophenone blank.

b) 1.43 ppm rhenium + reagent vs. acetophenone blank.

c) 1.43 ppm rhenium + reagent vs. reagent blank.

d) 1.43 ppm rhenium + reagent (without ammonium thiocyanate) vs. acetophenone blank.

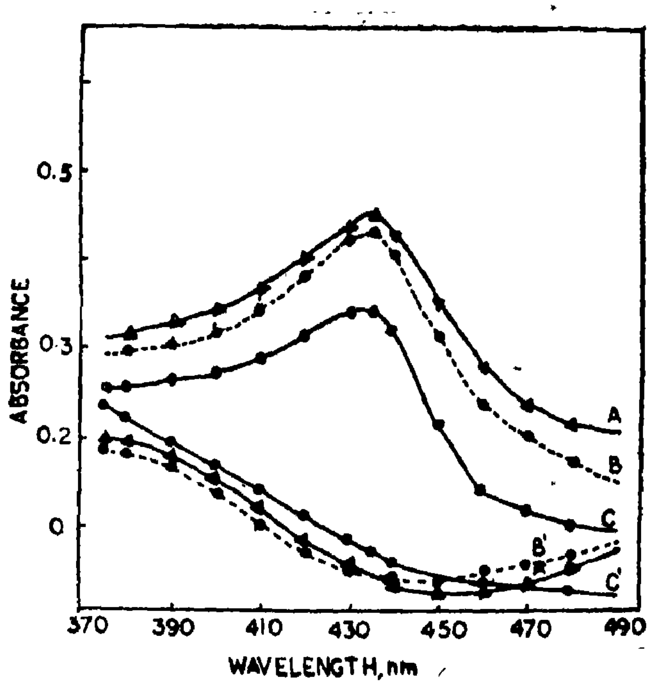


Fig. 2. Absorption spectra

(A', B', C') Reagent, 1 ml 10 *M* HCl, 2 ml 5% (W/V) ammonium thiocyanate, 1 ml 1% (W/V) substituted derivative of MBTP (5-hydroxy-8-nitro MBTP, 7-hydroxy-8-nitro MBTP and 5-hydroxy-6, 8-dinitro MBTP respectively) 1 ml stannous chloride vs. acetophenone blank.

(A, B, C) 2.86 ppm rhenium + reagent as above vs. acetophenone blank.

reagent blanks. The sensitivities of colour reactions in these cases were lower than that of rhenium-thiocyanate complex. Hence, these are not recommended for spectrophotometric determination of rhenium.

Interferences

The following ions were tolerated upto the amounts shown in brackets: As^{5+} and Sb^{3+} (50 folds); Cd^{2+}, Hg^{2+} and Bi^{3+} (100 folds); Ce^{4+} (500 folds); Mn^{2+}, Fe^{2+}, phosphate and borate (1000 folds); Na^{+}, K^{+}, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Pb^{2+}, Al^{3+}, La^{3+}, Ti^{4+}, Zr^{4+}, oxalate, chloride, citrate, tartrate and acetate (2000 folds). However, serious interferences were observed for Mo^{6+}, W^{6+}, U^{6+}, V^{5+}, Se^{4+}, Fe^{3+}, Ni^{2+}, Cu^{2+}, Ag^{+} and Tl^{+}; but the interference from Mo^{6+}, U^{6+}, V^{5+}, Se^{4+}, Ni^{2+} and Cu^{2+} can be eliminated by a tertiary amine-chloroform extraction[10] prior to the determination of rhenium. It was also found that the interference of Mo^{6+} can be avoided by extracting it as the pink molybdenum-MBTP complex into a 1 : 1 mixture of carbon tetrachloride and benzene, the procedure of which is mentioned below:

To a mixture containing 12.5 ppm of Re^{7+} and a known amount of Mo^{6+} in a separatory funnel, add 2 ml of 10 *M* HCl, followed by a slight excess of 1% (W/V) MBTP (approximately 0.05 g MBTP required for 25 μg of Mo^{6+}), shake well for 2 min. and let stand for about 5 min. for the pink colour to develop. Then add about 5 ml of the solvent mixture, shake well, allow layers to separate, drain the bottom solvent mixture layer and discard. If the aqueous layer has pink colour, repeat the extraction once more. Add a fresh quantity of reagent solution and test for completion of reaction. If pink colour is developed repeat the operations until further addition of reagent solution no longer produces a pink colour. The solvent mixture extracts excess of reagent also and the aqueous solution will be colourless after removal of molybdenum. Finally adjust the acidity of the aqueous medium to be 1.8 – 2.6 N and determine rhenium by the proposed method. The results are summarised in Table 1. The reagent MBTP behaves similarly to sodium ethyl xanthate[9] in separating molybdenum from solutions containing rhenium.

TABLE 1—DETERMINATION OF RHENIUM AFTER SEPARATION OF MOLYBDENUM BY THE PROPOSED EXTRACTION METHOD.

No.	Mo present ppm	Re taken ppm	Re found ppm
I	23.6	12.50	12.45
II	47.2	12.50	12.47
III	118.0	12.50	12.50
IV	236.0	12.50	12.45
V	1180.0	12.50	12.52
VI	2360.0	12.50	12.47

Applications

The proposed method was used for the determination of rhenium in synthetic mixtures, the composition and results of which are given in Table 2. The interferences from Mo^{6+}, W^{6+} and V^{5+} in the mixtures were eliminated by extraction with a solution of tertiary amine in chloroform.

TABLE 2—DETERMINATION OF RHENIUM IN SYNTHETIC MIXTURES

No.	Composition of mixtures	Re(VII) ppm added	Re(VII) ppm found*
I.	Mo^{6+}(20), W^{6+}(5), U^{6+}(5), V^{5+}(5), Si^{4+}(5), Bi^{3+}(5)	12.50	12.44
II.	Mo^{6+}(40), W^{6+}(10), U^{6+}(10), V^{5+}(10), Si^{4+}(10), Bi^{3+}(5)	12.50	12.40
III.	Mo^{6+}(60), W^{6+}(20), U^{6+}(20), V^{5+}(20), Si^{4+}(20), Bi^{3+}(5)	12.50	12.42

Numbers in brackets indicate the amount of metal in mg.

* average of two experiments.

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Chlorpromazine Hydrochloride as a New Redox Indicator in Cerimetry

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The optimum conditions for the successful use of chlorpromazine hydrochloride as redox indicator in the cerimetric titration of iron(II), molybdenum(V), hydroquinone and ascorbic acid in sulphuric, hydrochloric and acetic acid media have been developed. The indicator gives sharp reversible colour change at the equivalence point. Its formal redox and transitional potentials have been determined. Its sensitivity towards various oxidising agents are reported. It has certain advantages over the existing redox indicators in cerimetry.

CHLORPROMAZINE hydrochloride, CPH, 2-chloro-10 (3-dimethylamino-n-propyl) phenothiazine hydrochloride was used as redox indicator in vanadametry[1]. CPH was stated to be useless as redox indicator in cerimetry[2]. In the present communication the authors have made detailed investigations of the indicator properties of CPH and proposed it as a sensitive indicator in the titration of iron(II), molybdenum(V), hydroquinone and ascorbic acid with cerium(IV) sulphate.

Experimental

Reagents:

A 0.1% solution of CPH was prepared in doubly distilled water and stored in an amber bottle.

Approximately $0.05N$ and $0.01N$ solutions of molybdenum(V)[3] and hydroquinone[4] were prepared and standardised against cerium(IV) sulphate solution.

Approximately $0.1N$ ascorbic acid solution was prepared by dissolving the requisite quantity of analar ascorbic acid (S. Merck) in one litre of metal free doubly distilled water containing 0.5 g of analar EDTA and 4 g of analar formic acid. The solution was standardised against potassium iodate[5].

Apparatus:

The potentiometric assembly consisted of a direct reading potentiometer, a mirror galvanometer, a bright platinum gauze indicator electrode, a saturated calomel reference electrode and an agar salt bridge. The titration mixture was stirred by a magnetic stirrer.

General Procedures :

Determination of the formal and transition potentials of CPH:

The formal redox potential of CPH was determined by the method of Schilt[6]. The transition potentials of CPH in the titration of iron(II) with cerium(IV) sulphate in acetic acid medium were determined by the potentiometric method[1].

Determination of sensitivity of CPH towards various oxidizing agents:

The sensitivity of CPH towards various oxidizing agents was determined by mixing a drop of vanadate, bromate, iodate, dichromate, cerium(IV) sulphate or ferricyanide, a drop of $2N$ hydrochloric acid and a drop of 1% CPH solution in a spot plate. Each test was allowed to stand for 30 sec. The results are given in Table 1.

TABLE 1—SENSITIVITY OF CPH TOWARDS SIX OXIDISING AGENTS

Oxidant	V^{5+}	BrO_3^-	$Cr_2O_7^{2-}$	Ce^{4+}	IO_3^-	$[Fe(CN)_6]^{3-}$
Identification limit (μg)	0.0456	0.056	0.064	0.134	0.385	1.133
Dilution limit	1:5.855x10^6	1:4.764x10^6	1:1.709x10^6	1:1.99x10^6	1:6.928x10^4	1:23.61x10^4

Cerimetric titration of iron(II), molybdenum(V), hydroquinone and ascorbic acid:

20 ml of 0.05-0.01N iron(II), molybdenum(V) or hydroquinone, 1 ml of 0.1% CPH indicator and phosphoric acid were diluted to 40 ml with sulphuric, hydrochloric or acetic acid and titrated with 0.05-0.01N cerium(IV) sulphate solution to the appearance of pink or orange-red colour.

20 ml of 0.1-0.05N ascorbic acid and 1 ml of 0.1% CPH were diluted to 40 ml with sulphuric, acetic, hydrochloric or phosphoric acid and titrated with cerium(IV) sulphate. CPH is added near the end-point in hydrochloric acid medium. The titration conditions, colour changes at the end-points and results are given in Table 2.

indicator must have suitable redox and transition potentials which should lie within the potential break in the potentiometric titration curve. The selected indicator should have a colour change at the potential as close possible to the equivalence point. Of the three methods used for determining the redox potential of a redox indicator, the methods of Bishop and Crawford[11] and Smith and Banick[12] failed to give the accurate value for the redox potential of CPH. The method of Schilt[6] was used to find the redox potential of CPH in varying concentration of sulphuric acid at 20°. A plot of potential versus time in different concentrations of sulphuric acid showed that the formal potential decreases very slowly with increasing time and acid concentration. The potentials extrapolated to zero time in 0.25, 0.50, 0.75, 1.00, 1.25 and 1.5M sulphuric acid were found to be 799, 788, 760, 753, 732 and 721 mV respectively. The values were accurate to ± 5 mV.

TABLE 2—CERIMETRIC DETERMINATION WITH CPH INDICATOR

Sl. No.	Reductant taken (mg)	Medium	Normality of Cerium(IV) sulphate	Reductant determined (mg)	Colour change at the end-point
1)	Iron(II)	3-6 ml of 10M H_3PO_4 + 0.50 - 1.0M		Iron(II)	Almost colourless
	113.71	H_2SO_4 or HCl/0.5-2.5M HAc	0.1	113.71	to pink
	55.73	—do—	0.05	55.73	—do—
	5.70	—do—	0.01	5.71	
2)	Molybdenum(V)			Molybdenum(V)	
	193.8	1-4 ml of 10M H_3PO_4 + 0.2-0.5M H_2SO_4/1.0-2.0M HCl/0.5-3.0M HAc	0.1	193.8	Colourless
	94.76	—do—	0.05	94.76	to pink
	9.70	—do—	0.01	9.71	
3)	Hydroquinone	2-4 ml of 10M H_3PO_4 + 0.5-1.0M			Light yellow to
	111.5	H_2SO_4/0.5-0.7M HCl/0.6-3.0M HAc	0.1	111.5	orange red
	55.38	—do—	0.05	55.38	
	5.43	2-4 ml of 10M H_3PO_4 + 0.5-1.0M H_2SO_4	0.01	5.44	
4)	Ascorbic acid				Colourless
	166.2	2-6 ml of 10M H_3PO_4 + 1-2M HAc/0.5-1.0M H_2SO_4	0.1	166.2	to pink
	88.49	—do—	0.05	88.51	—do—
	166.2	2-3 ml of 10M H_3PO_4 + 1-2M HCl	0.1	166.2	Colourless
	88.38	—do—	0.05	88.40	to pink
	166.8	1-2M H_3PO_4	0.1	166.8	—do—
	83.59	—do—	0.05	83.60	—do—
	17.60	—do—	0.01	17.62	—do—
	8.49	—do—	0.01	8.51	
	4.12	—do—	0.005	4.13	
	2.18	—do—	0.005	2.19	
	0.8	—do—	0.002	0.82	
	0.4	—do—	0.002	0.42	

Results and Discussion

CPH is highly soluble in water giving colourless solution which is stable for about a week at room temperature (27°) and for three months at low temperature (8°). It undergoes reversible one electron oxidation to a red intermediate[7,8] which is believed to be a radical cation[9,10]. The radical cation is irreversibly oxidized to a colourless sulphoxide[9] with the loss of one more electron.

Determination of the formal redox and transition potentials:

It is necessary when choosing a redox indicator for a particular redox titration to ensure that its formal redox potential lies within those of redox systems. The

It is not possible to get accurate values for the transition potentials of CPH in the titration of iron(II) with cerium(IV) sulphate in sulphuric or hydrochloric acid medium as the potential at which CPH gives the first trace of end-point pink colour is not stabilised. However the steady transition potentials are obtained in acetic acid medium 90 seconds after the addition of the last drop of cerium(IV) sulphate which marks the end-point. The transition potentials of CPH in the titration of iron(II) with cerium(IV) sulphate in 0.50, 1.00, 1.50, 2.0 and 2.5M acetic acid solution containing 0.25M phosphoric acid and 0.25M sulphuric acid, were found to be 760, 756, 752, 748 and 745 ± 5 mV respectively at 28°. The values of the redox and transition

potentials of CPH indicate that CPH serves as a good indicator in the titration of iron(II), molybdenum(V), hydroquinone and ascorbic acid with cerium(IV) sulphate.

The results in Table 1 shows that the sensitivity of CPH towards six oxidising agents is $V^{5+} > BrO_3^- > Cr_2O_7^{2-} > Ce^{4+} > IO_3^- > [Fe(CN)_6]^{3-}$.

Titration of 0.1-0.01N iron(II) ammonium sulphate

CPH does not give sharp end-points in the titration of iron(II) with cerium(IV) sulphate in hydrochloric, sulphuric or acetic acid medium because of the slow reduction of the red radical cation by iron(II). It gives sharp and correct end-points in 0.5-1.0*M* sulphuric or hydrochloric or 0.5-2.5*M* acetic acid solution containing 3-6 ml of 10*M* phosphoric acid in a total volume of 60 ml. Sluggish end-points are obtained at acidities higher than 1.0*M* sulphuric or hydrochloric acid even in the presence of phosphoric acid. Premature end-points and precipitation are obtained in acetic acid medium stronger than 2.5*M*. Phosphoric acid (10*M*) less than 3 ml gives sluggish end-points and more than 6 ml gives premature end-points. The colour change at the end-point is from almost colourless to pink. The end-point colour is stable for more than 10 hours.

It was found that 0.8-2.0ml of 0.1% CPH solution is necessary in a total volume of 60 ml for proper indicator action. Higher concentration of the indicator gives higher titre values.

The indicator correction needed for CPH has been found by comparing the results from the potentiometric titrations with those when CPH was used. The average indicator correction is 0.02 ml of 0.01*N* cerium(IV) sulphate for 1 ml of 0.1% CPH solution.

Experiments have shown that stannic chloride, mercuric chloride and mercurous chloride do not interfere with the function of CPH indicator in the titration of iron(II) with cerium (IV) sulphate. CPH can therefore be usefully employed in the determination of iron(III) present in ferric alum or in haematite after the conventional method of reduction of iron(III) by stannous chloride.

CPH is superior to ferroin indicator in that it is more sensitive requiring less indicator correction and it works in the presence of acetic acid.

Titration of 0.1-0.01N molybdenum(V)

Ferroin[8,13,14], diphenylbenzidine[15] (DB) and many other indicators were proposed in the titration of molybdenum(V) with cerium(IV) sulphate. Ferroin which is most commonly used in cerimetry functions only in 3*M* hydrochloric acid in the presence of syrupy phosphoric acid[15]. Grubitsch et al[16] proposed 4*M* hydrochloric acid for using ferroin indicator. DB works in 4*M* hydrochloric acid.

CPH gives sharp colour change from colourless to pink at the equivalence point in acid media ranging from 1-2.0*M* hydrochloric, 0.2-0.5*M* sulphuric or 0.5-3.0*M* acetic acid solution containing 1-4 ml of 10*M* phosphoric acid in a total volume of 60 ml. The indicator gives unstable end-points at higher acidities. 0.8-2.0 ml of 0.1% CPH is required for proper indicator action in a total volume of 60 ml. With lower and higher concentration of CPH indicator, the end-points are sluggish and are not easily reversible. The end-point colour is stable for 15-150 min. in 0.5-0.2*M* sulphuric acid, 60-120 min. in 2.0-1.0*M* hydrochloric acid and 20-25 min. in acetic acid medium.

CPH is superior to ferroin in that i) it works at lower acidities, ii) it is more sensitive requiring less indicator correction and iii) it functions satisfactorily in acetic acid medium.

Titration of 0.1-0.01N hydroquinone

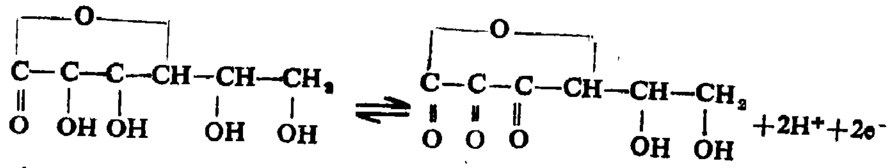
Diphenylamine[17], methyl red[17], ferroin[18], Rhodamine 6G (Rh)[19], NPA[19], crystal violet[19] (CV), alphazurin G[20], *p*-ethoxy chrysiodine[21], setopalin[22], eriogreen[22], erioglaucine[22] and promethazine hydrochloride[23] were proposed as indicators in this titration. Most of these indicators are unsatisfactory for one reason or another. Diphenylamine requires a large indicator correction to bring the values in agreement with potentiometric values. Methyl red is added near the end-point and the colour change is not satisfactory. Rh, NPA and CV work in the titration with only 0.05*N* cerium (IV) sulphate. Setopalin, eriogreen, erioglaucin are added in the beginning and near the end-point of the titration and the end-point colour is stable only for a few seconds. Ferroin needs an indicator correction of 0.1 ml of 0.01*N* cerium(IV) sulphate.

CPH gives sharp and correct end-points in 0.5-1.0*M* sulphuric, 0.5-0.7*M* hydrochloric or 0.6-3.0*M* acetic acid solution containing 2-4ml of 10*M* phosphoric acid in a total volume of 60 ml. It gives a reversible colour change from light yellow to orange red at the equivalence point. The end-point colour is stable for 10-5 min. in 0.5-1.0*M* sulphuric, 10 min in 0.5-0.7*M* hydrochloric and 30-20 min in acetic acid media. It gives sluggish and premature end-points at higher acidities of sulphuric, hydrochloric and phosphoric acid because of the slow reduction of the oxidized indicator by hydroquinone. Higher concentration of acetic acid leads to precipitation. 0.8-2.0 ml of 0.1%CPH is required for proper indicator action in a total volume of 60 ml. With higher concentrations of CPH over-titration occurs.

CPH has many advantages over most of the existing redox indicators in that 1) it is more sensitive requiring less indicator correction, 2) it works in acetic acid medium and (3) the end-point colour is more stable.

Titration of 0.1-0.05N ascorbic acid

The determination of ascorbic acid is of great importance because of its extensive use as vitamin 'c'. and reducing titrant. It is oxidized to dehydroascorbic acid by cerium(IV) sulphate with the loss of two electrons as follows :



Ferroin, barium diphenylaminesulphonate (DS), NPA and Rh[24] were proposed in the titration of 0.1*N* ascorbic acid in 0.75-1.50*M* sulphuric acid solution containing 1 ml of syrupy phosphoric acid. Rh requires day light to give greenish fluorescence which is quenched by slight excess of cerium(IV) sulphate. With ferroin, cerium(IV) sulphate should be added in fractions of a drop with the aid of a thin glass rod near the end-point. DS and NPA give varying results with varying concentrations of indicators. CPH indicator gives sharp colour change from colourless to pink at the equivalence point in 1-2*M* acetic or 0.5-1.0*M* sulphuric acid solution containing 2-6 ml of 10*M* phosphoric acid in a total volume of 60 ml. The end-point colour is stable for about 50 minutes. Precipitation is seen in higher concentration of acetic acid and unstable end-points are obtained in higher concentration of sulphuric acid. CPH gives sharp end-points in hydrochloric acid media ranging from 1.0-2.0*M* in the presence of 2-3 ml of 10*M* phosphoric acid. To get stable and bright end-points, 1 ml of CPH should be added near the end-point. Higher concentrations of phosphoric acid give premature end-points and lower concentrations give sluggish end-points. The end-point colour is stable for about 60-40 minutes.

It was found that 0.8-2.0 ml of 0.1% CPH in acetic acid and 1.0-2.5 ml in hydrochloric or sulphuric acid media are necessary for proper indicator action in a total volume of 60 ml. Higher concentration of CPH leads to slightly higher titre values.

Titration of ascorbic acid in phosphoric acid medinm

Phosphoric acid has some advantages over sulphuric, hydrochloric or acetic acid as titration medium. It reduces the formal potential of cerium(IV)/cerium(III) system to a value of 1.22V[25]. The redox potential of ascorbic acid-dehydroascorbic acid is reported to be 185 mV in a solution of *p*H 7 and − 12 mV to + 326 mV in a solution of *p*H range 8.7 – 1.05[26]. This redox potential increases to 445-464 mV in 1-2*M* phosphoric acid[24]. This increased potential affords protection to the ascorbic acid against atmospheric oxidation. Moreover, phosphoric acid complexes any heavy metal ions present which catalyze the atmospheric oxidation of ascorbic acid. Hence very small amounts of ascorbic acid can be determined in phosphoric acid medium. Ferroin[26] functions only in 12-13*M* phosphoric acid. CPH gives sharp colour change from colourless to pink at the equivalence point in the titration of ascorbic acid (1.0-170 mg) with 0.002-0.1*N* cerium(IV) sulphate in 1-2*M* phosphoric acid solution. Below this range of acid premature end-points are obtained. Above this range overtitration occurs. The end point colour is stable for about 70 min.

It was found that 0.8-2.0 ml of 0.1% CPH is necessary in the titration of ascorbic acid with 0.1-0.05*N* cerium(IV) sulphate for proper indicator action in a total volume of 60 ml. 0.4-0.7 ml of 0.1% CPH is necessary in the titration with 0.01-0.002*N* cerium(IV) sulphate for proper indicator action in a total volume of 35 ml.

CPH can be used for the determination of ascorbic acid in the presence of ten-fold excess of oxalic, citric, tartaric, succinic and malic acids, glucose, fructose and sucrose in phosphoric acid medium as these organic compounds do not interfere. It can also be used in sulphuric, hydrochloric or acetic acid media in presence of these organic compounds except oxalic acid.

Comparison with other indicators

CPH has advantages over NPA and DS in that i) it gives sharper end-points and more accurate values, ii) it functions in four acid media while NPA, DS and Rh function only in sulphuric acid medium and iii) it has less indicator correction. It is superior to ferroin because i) it works in 1-2*M* phosphoric acid medium, ii) it functions in hydrochloric and acetic acid media, iii) it has smaller indicator correction and (iv) it gives sharper end-points.

Determination of ascorbic acid in citrus fruit juices

Ascorbic acid present in citrus fruit juices has been determined by a number of chemical methods[27-28] in which no internal indicator has been used.

The extraction of juice from citrus fruits like lemons and oranges should be done quickly to prevent aerial oxidation of ascorbic acid before analysis. A known volume of the extracted juice is immediately diluted to 25 ml with phosphoric acid so as to give 3*M* with respect to phosphoric acid which prevents aerial oxidation. The solution is titrated with 0.005*N* cerium(IV) sulphate using 1 ml of 0.1% CPH to the appearance of pink colour.

The results of the cerium(IV) sulphate method compare very favourably with those obtained by the indophenol method. The proposed method has the advantages of sharper end-points, increased stability of the reagents, greater simplicity and rapidity and more reproducible results.

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Kinetics and Mechanism of Oxidation of Some Aldopentoses by Quinquevalent Vanadium in Sulphuric Acid

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The oxidation of D-xylose, L-arabinose and D-ribose by quinquevalent vanadium in sulphuric acid medium has been found to be of first order with respect to both oxidant and substrate concentrations. The rate of oxidation has been found to increase with first power of $[H^+]$ in 2.0M to 4.5M acid concentration range and with second power of $[H^+]$ in higher acid range>4.5M at constant HSO_4^- concentration. The increase in oxidation rate with HSO_4^- concentration at constant H^+ concentration has been also observed. The thermodynamic parameters have been evaluated from Arrhenius plots. The effect of changing the composition of acetic acid—water binary mixture on rate has indicated the reaction to be ion-dipole type. Possible reaction steps have been also proposed.

KINETICS of oxidation of carbohydrates, mainly of hexoses has been studied by various oxidants, including the ions of higher valent transition metals like Ce(IV)[1,2,3], Co(III)[4], Mn(III)[5]. In comparison of hexoses, the kinetics of oxidation of pentoses, which constitute an important category of monosaccharides has been studied by few oxidants like Br_2 water in alkaline medium[6], chloramine-T[7], Cu(II) in alkaline medium[8], Ag(I) in alkaline medium[9]. Amongst the various transition metal ions used for oxidation studies, quinquevalent vanadium in acid medium is a most versatile and potent oxidant and has been used for oxidation studies of various organic compounds[10] including hexoses[11]. The present work deals with the oxidation of some aldopentoses like D-xylose, L-arabinose and D-ribose by quinquevalent vanadium to evaluate the general feature of oxidation process in sulphuric acid medium and steps involved in it.

Experimental

Vanadium (V) solution was prepared by dissolving ammonium meta vanadate (Reidel) in appropriate concentration of sulphuric acid (Analar/B.D.H.). Solutions of aldopentoses (E. Merck/B.D.H.) were prepared fresh daily. Other various chemicals used like sodium bisulphate, sodium sulphate, acetic acid N-phenyl anthranilic acid, chromotropic acid etc. were of Analar/B.D.H. grade.

Oxidation reactions were followed by quenching aliquots withdrawn at regular known interval of time in ice cold titration flask containing 5 ml. of 5N sulphuric acid and estimating unreacted vanadium(V) with a standard solution of Mohr's salt using N-phenyl anthranilic acid as an indicator.

Results

All the three aldopentoses consumed ~2 equivalents of vanadium (V) in 3.5 M sulphuric acid in 24 hours at 40° under the condition of kinetic run. The reaction can be represented stoichiometrically by equation (1)

$$C_5H_{10}O_5 + 2V(V) + H_2O \rightarrow HCOOH + 4HCHO + 2V(IV) + 2H^+ \quad (1)$$

In presence of excess of vanadium (V) (~20 folds), it was found that one equivalent of aldopentose required ten equivalents of vanadium (V) for complete oxidation (~10 days) in each case. Thus, the overall oxidation reaction can be represented by equation (2)

$$C_5H_{10}O_5 + 10V(V) + 5H_2O \rightarrow 5HCOOH + 10H^+ + 10V(IV) \quad (2)$$

The formation of HCHO as intermediate product was confirmed with usual tests and with chromotropic acid spot test also.[12(a)] After the completion of reaction the formation of HCOOH was also confirmed by mercuric chloride and chromotropic acid spot test[12(b)]. The formation of free radicals during the course of reaction was confirmed by the induced polymerisation reaction of acrylyn-H monomer (Asian Acrylates, Bombay).

TABLE 1—VARIATION OF RATE CONSTANT WITH ALDOPENTOSE CONCENTRATION

A. [Vanadium(V)] = 1.0×10^{-3} M, [H_2SO_4] = 3.5 M, Temp. = 45°
B. [Vanadium(V)] = 1.0×10^{-3} M, [H_2SO_4] = 3.5 M, Temp. = 40°
C. [Vanadium(V)] = 1.0×10^{-3} M, [H_2SO_4] = 3.5 M, Temp. = 40°

[Aldopentose] $M \times 10$	A		B		C	
	$10^4 k_1$ s^{-1}	$10^4 k_1$/[D-xylose] l mole^{-1} s^{-1}	$10^4 k_1$ s^{-1}	$10^4 k_1$/[D-arabinose] l mole^{-1} s^{-1}	$10^4 k_1$ s^{-1}	$10^4 k_1$/[D-ribose] l mole^{-1} s^{-1}
1.0	1.38	13.80	0.69	6.90	0.97	9.70
2.0	2.57	12.85	1.37	6.85	1.91	9.55
3.0	4.34	14.46	1.89	6.30	3.13	10.43
4.0	5.26	13.15	2.54	6.35	3.83	9.57
5.0	6.69	13.38	3.30	6.60	5.00	10.00
6.0	8.13	13.55	3.85	6.42	—	—

Ave. $\frac{10^4 k_1}{[\text{D-xylose}]} = 13.53 \pm 0.40$ Ave. $\frac{10^4 k_1}{[\text{L-arabinose}]} = 6.57 \pm 0.21$ Ave. $\frac{10^4 k_1}{[\text{D-ribose}]} = 9.85 \pm 0.29$

The kinetic studies were performed by taking aldopentose and sulphuric acid in sufficient excess over the vanadium (V) concentration. It was observed that the rate of disappearance of vanadium (V) followed first order kinetics uniformly. The pseudo first order rate constants (k_1) were evaluated from the integrated form of first order rate equation. The order with respect to aldopentose has been also found to be one (Table 1). Further, linear graphs passing through origin can be obtained if drawn between $1/k_1$ and 1/[aldopentose] showing no kinetic evidence for intermediate compound formation between vanadium (V) and aldopentose.

In preliminary studies rate constant has been found to increase exponentially with sulphuric acid concentration and activity computed from activity coefficient data[13] (Table 2). For finding out the dependence of rate constant on H^+ concentration at constant [HSO_4^-] and on HSO_4^- concentration at constant [H^+], the rate studies were performed in two different H^+ concentration ranges. In lower H^+ concentration range (2.0 M to 4.5 M) the rate constant has been found to depend on first power of H^+ concentration, whereas in higher H^+ concentration, range (5.0 M to 8.0 M) a second power dependence on [H^+] has been observed (Table 3). Further, an increase in rate constant with HSO_4^- concentration has been also observed in both acid ranges (Table 4).

From the data given in Table 3 linear graphs with negative slope values can be obtained if drawn between log k_1 and H_0 (values taken from Paul and Longs' Table[14]) in all the three cases and in two different ranges. Further, from the linear plots obtained between log $k_1 + H_0$ and log aH_2O[15] "ω" values have been computed as 8.0, 7.0 and 7.0 in lower acid concentration range and 3.0, 3.2 and 2.8 in higher acid concentration range for D-xylose, L-arabinose and D-ribose respectively.

TABLE 2—DEPENDENCE OF RATE CONSTANT ON SULPHURIC ACID CONCENTRATION

A [Vanadium(V)] = 1.0×10^{-3} M, [D-xylose] = 1.0×10^{-1} M [Temp. = 40°
B [Vanadium(V)] = 1.0×10^{-3} M, [L-arabinose] = 1.0×10^{-1} M Temp. = 40°
C [Vanadium(V)] = 1.0×10^{-3} M, [D-ribose] = $1.0 \times 10^{-1} M$ Temp. = 40°

[H_2SO_4] M	a±	A $10^4 k_1$ s^{-1}	B $10^4 k_1$ s^{-1}	C $10^4 k_1$ s^{-1}
2.0	0.21	0.56	0.38	0.65
3.0	0.35	0.81	0.53	1.02
4.0	0.67	1.12	0.72	1.62
5.0	0.84	1.94	1.27	2.45
6.0	1.23	2.55	1.89	5.26
8.0	2.27	7.21	4.83	12.10

TABLE 3—DEPENDENCE OF RATE CONSTANT ON H^+ CONCENTRATION AT CONSTANT $[HSO_4^-]$

Lower range

A [Vanadium(V)] = $1.0 \times 10^{-3} M$, [D-xylose] = $1.0 \times 10^{-1} M$ $[HSO_4^-]$ = 4.5 *M* ; Temp. = 45°

B [Vanadium(V)] = $1.0 \times 10^{-3} M$, [L-arabinose] = $1.0 \times 10^{-1} M$ $[HSO_4^-]$ = 4.5 *M* ; Temp. = 40°

C [Vanadium(V)] = $1.0 \times 10^{-3} M$, [D-ribose] = $1.0 \times 10^{-1} M$ $[HSO_4^-]$ = 4.5 *M* ; Temp. = 40°

$[H^+]$ *M*	A $10^4 k_1$ s^{-1}	B $10^4 k_1$ s^{-1}	C $10^4 k_1$ s^{-1}
2.0	0.86	—	—
2.5	1.06	0.48	0.69
3.0	1.26	0.56	0.82
3.5	1.47	0.62	0.96
4.0	2.10	0.72	1.12
4.5	2.44	0.88	1.26

Higher range

A [Vanadium(V)] = $1.0 \times 10^{-3} M$, [D-xylose] = $1.0 \times 10^{-1} M$ $[HSO_4^-]$ = 8.0*M* ; Temp. = 34°

B [Vanadium(V)] = $1.0 \times 10^{-3} M$, [L-arbinose] = $1.0 \times 10^{-1} M$ $[HSO_4^-]$ = 8.0 *M* ; Temp. = 35°

C [Vanadium(V)] = $1.0 \times 10^{-3} M$, [D-ribose] = $1.0 \times 10^{-1} M$ $[HSO_4^-]$ = 8.0 *M* ; Temp. = 35°

$[H^+]$ *M*	A $10^4 k_1$ s^{-1}	B $10^4 k_1$ s^{-1}	C $10^4 k_1$ s^{-1}
5.0	0.49	0.66	1.04
6.0	0.84	0.78	1.55
7.0	1.08	1.13	2.09
8.0	1.52	1.45	2.53

It has been also observed that rate constant increases inversely with dielectric constant of medium varied by taking binary mixtures of acetic acid-water of different compositions (Table 5). The dielectric constants of such mixtures have been computed by assuming approximate validity of mixture law[16] at the temperature of study.

A linear plot if drawn between log k_1 and 1/D can be obtained with a positive slope showing the reaction under study to be of ion dipole type. It can be assumed that aldopentose molecule behaves as dipole in aqueous medium whereas positive ionic species of vanadium (V) can be considered to be active in the reaction.

TABLE 4—DEPENDENCE OF RATE CONSTANT ON HSO_4^- CONCENTRATION AT CONSTANT $[H^+]$

Lower range

A [Vanadium(V)] = $1.0 \times 10^{-3} M$, [D-xylose] = $1.0 \times 10^{-1} M$ $[H^+]$ = 3.5 *M* ; Temp = 45°

B [Vanadium(V)] = $1.0 \times 10^{-3} M$, [L-arabinose] = $1.0 - 10^{-1} M$ $[H^+]$ = 3.5 *M* ; Temp. = 40°

C [Vanadium(V)] = $1.0 \times 10^{-3} M$ $[H^+]$ = 3.5 *M* [D-ribose] = $10 \times 10^{-1} M$; Temp. = 40°

$[HSO_4^-]$ *M*	A $10^4 k_1$ s^{-1}	B $10^4 k_1$ s^{-1}	C $10^4 k_1$ s^{-1}
3.5	1.25	0.69	1.07
4.0	1.37	0.82	1.24
4.5	1.59	0.99	1.44
5.0	1.80	—	—
5.5	1.92	1.28	1.74

Higher range

A [Vanadium(V)] = $1.0 \times 10^{-3} M$, [D-xylose] = $1.0 \times 10^{-1} M$ $[H^+]$ = 6.0*M* ; Temp. = 35°

B [Vanadium(V)] = $1.0 \times 10^{-3} M$, [L-arbinose] = $1.0 \times 10^{-1} M$ $[H^+]$ = 6.0 *M* ; Temp. = 35°

C [Vanadium(V)] = $1.0 \times 10^{-3} M$, [D-ribose] = $1.0 \times 10^{-1} M$ $[H^+]$ = 6.0 *M* ; Temp. = 35°

$[HSO_4^-]$ *M*	A $10^4 k_1$ s^{-1}	B $10^4 k_1$ s^{-1}	C $10^4 k_1$ s^{-1}
6.0	0.81	0.63	1.69
6.5	0.97	0.82	2.20
7.0	1.29	0.96	2.63
8.0	1.84	1.27	3.30

TABLE 5—DEPENDENCE OF RATE CONSTANT ON ACETIC ACID-WATER COMPOSITION

A [Vanadium(V)] = $1.0 \times 10^{-3} M$, [D-xylose] = $1.0 \times 10^{-1} M$ $[H_2SO_4]$ = 1.81 *M* ; Temp. = 40°

B [Vanadium(V)] = $1.0 \times 10^{-3} M$, [L-arabinose] = $1.0 \times 10^{-1} M$ $[H_2SO_4]$ = 1.35 *M* ; Temp. = 40°

C [Vanadium(V)] = $1.0 \times 10^{-3} M$, [D-ribose] = $1.0 \times 10^{-1} M$ $[H_2SO_4]$ = 1.61 *M* ; Temp. = 40°

Acetic acid %	10^3 D	A $10^4 k_1$ s^{-1}	B $10^4 k_1$ s^{-1}	C $10^4 k_1$ s^{-1}
30	18.81	1.45	1.26	1.23
40	21.53	2.66	2.34	2.34
50	25 17	4.59	3.84	4.72
60	30.36	10.94	7.31	8.90
70	38.04	30.66	19.88	22.23

TABLE 6—DEPENDENCE OF RATE CONSTANT ON TEMPERATURE

A [Vanadium(V)] = 1.0×10^{-2} *M* [D-xylose] = 1.0×10^{-1} *M* [H_2SO_4] = 3.5 M
B [Vanadium(V)] = 1.0×10^{-2} *M* [L-arabinose] = 1.0×10^{-1} *M* [H_2SO_4] = 3.5 M
C [Vanadium(V)] = 1.0×10^{-2} *M* [D-ribose] = 1.0×10^{-1} *M* [H_2SO_4] = 3.5 M

	$10^4 \times k_1/s^{-1}$					$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta G^{\neq}$ at 313°K
	35°	40°	45°	50°	55°	K. cal. mole^{-1}	e.u.	K. cal./mole
A	0.45	0.53	1.40	1.93	4.23	21.46	−6.63	23.53
B	0.44	0.67	1.24	2.23	3.72	22.80	−2.44	23.50
C	0.68	0.98	1.98	3.21	5.31	20.79	−8.04	23.25

Many earlier studies[17,18,19,20] have indicated that the form of the vanadium(V) active species depend on acid types and their concentration ranges. If VO_2^+ is considered as an initial species of vanadium(V) in acidic medium, then from the dependence of rate constant on [H^+] and increase in rate constant with [HSO_4^-] in lower acid concentration range ($\leqslant 4.5M$), the active species of vanadium(V) in this range can be designated by considering the following equilibria[17,21,22]

$$VO_2^+ + H_3O^+ + HSO_4^- \rightleftharpoons \underset{A}{[V(OH)_3HSO_4]^+} \quad (3)$$

Similarly from the results obtained in higher acid concentration range (>4.5 *M*) the following equilibria can be considered to be operative[23] for the formation of active species in this range

$$VO_2^+ + 2H^+ + 2HSO_4^- \rightleftharpoons \underset{B}{[V(OH)_2(HSO_4)_2]^+} \quad (4)$$

The data on dependence of rate constant on temperature has been summarised in Table 6. The activation parameters evaluated from Arrhenius plots have also been given.

A linear isokinetic plot with β value 340° K can be obtained if drawn between $\Delta H^{\neq}$ and $\Delta S^{\neq}$, showing that the oxidation reaction under study is both energy and entropy controlled obeying Leffler's compensation law[24]. Hence, an identical oxidation mechanism for D-xylose, L-arabinose and D-ribose can be proposed.

Vanadium(V) is present in two cases, that is, in lower and higher acid concentration range as A and B shown in equation 3 and 4 and hence the first step of oxidation can be shown either as 5(a) or (b).

$$\text{CHO.CHOH.CHOH.CHOH.CH}_2\text{OH} + [V(OH)_3HSO_4]^+ \xrightarrow{\text{Slow}} R^{\cdot} + V(IV) + H^+ + HCHO \quad 5(a)$$

or

$$\text{CHO.CHOH.CHOH.CHOH.CH}_2\text{OH} + [V(OH)_2(HSO_4)_2]^+ \xrightarrow{\text{Slow}} R^{\cdot} + V(IV) + H^+ + HCHO \quad 5(b)$$

or in general

$$\text{CHO.CHOH.CHOH.CHOH.CH}_2\text{OH} + V(V) \xrightarrow{\text{Slow}} R^{\cdot} + V(IV) + H^+ + HCHO \quad (5)$$

where $R^{\cdot}$ is CHO.CHOH.CHOH.ĊHOH

The free radical CHO.CHOH.CHOH.ĊHOH thus formed breaks further in a chain mechanism to formic acid and formaldehyde as :

$$\text{CHO.CHOH.CHOH.\dot{C}HOH} + V(V) + H_2O \xrightarrow{\text{Fast}} HCOOH + 3HCHO + H^+ + V(IV) \quad (6)$$

The formaldehyde formed in steps (5) and (6) can further be oxidised to formic acid, if excess of oxidant is present as follows:

$$4HCHO + 8V(V) + 4H_2O \xrightarrow{\text{Fast}} 4HCOOH + 8V(IV) + 8H^+ \quad (7)$$

The above proposed steps of oxidation mechanism incorporate the results obtained during the studies.

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Application of Differential Electrolytic Potentiometry to the Titration of Iodate Ion with Ferrous Ion in Different Acid Solutions

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Differential electrolytic potentiometry of the reaction between potassium iodate in hydrochloric, sulphuric and phosphoric acid solutions and ferrous ion is reported in this communication. Accurate titrations are possible in the three acid solutions of moderate concentrations, but the mechanism of reduction of IO_3^- by Fe^{2+} appear to be different in each. In hydrochloric acid solutions, the differential titration curves show one single peak corresponding to the formation of ICl_3. In sulphuric and phosphoric acid solutions the number of peaks in the titration curve increase to two and three respectively, indicating intermediate formation of I^{3+} species in both, which is subsequently reduced to iodine. In phosphoric acid, iodine is further reduced and the third peak indicates the reduction of iodate ion ultimately to iodide ion. An additional peak appears when the titrations in sulphuric and phosphoric acid solutions are carried out in presence of potassium chloride. This peak at 4 moles of titrant corresponds to the formation of ICl during the course of reduction. Optimum conditions for the titrations are discussed.

DIFFERENTIAL electrolytic potentiometry affords a method of investigating both total and partial reaction. Bishop[1,2] has examined in detail the applicability of this method to redox titrimetry and he, as well as Reilley, Cooke and Furman[3], carried out a number of titrations in this context including those involving the reduction of Ce^{4+}, $Cr_2O_7^{2-}$ and MnO_4^- by Fe^{2+}. Classical zero-current potentiometric titration of IO_3^- by Fe^{2+} was found to be feasible by the authors[4] in high acid concentrations only, who also found that reduction of IO_3^- in hydrochloric acid solutions resulted in the formation of ICl_3 and then ICl. Some of the advantages of differential electrolytic potentiometry being high rates of potential equilibriation and accurate location of a succession of end points, the method was applied in the present work in an attempt to understand the mechanism of reduction of iodate ion and to see whether titrations with Fe^{2+} in lower acid concentrations are possible. Accordingly the lower limit of hydrochloric, sulphuric and phosphoric acid solutions in which titrations were done was 1N to 2N, below which titrations were not feasible.

Experimental

The apparatus used were essentially those described by Van Name and Fenwick[5]. A pair of identical platinum wires, 5mm long (at times wires of greater length had to be used) and 0.25mm diameter served as the stationary indicator electrodes, the differential potential, E_Δ, across which was measured by a high input resistance potentiometer (Cambridge bench type *p*H meter). The electrodes were connected in series with ballast resistors (half-watt carbon radio resistors) of 20 to 100 megohms. Current source was a battery of dry cells of 100 volts and a minute (L1μA to 5μA) heavily stabilised polarising current was thus continuously passed through the pair of indicator electrodes immersed in the titration solution. As low stirring rate affects the differential potential and a constant potential is reached only when the rate is sufficiently high,[6] the solution was stirred at a constant rate at just below cavitation speed by using a magnetic (at times a mechanical) stirrer. Stable potential readings were rapidly attained in most cases. The titration cell contained 150 ml. of 0.001 *M* KIO_3, in different acid solutions (of varying strengths) as supporting electrolytes. The titrant solution (for titrations in sulphuric acid solutions), 0.1*M* $FeSO_4.(NH_4)_2SO_4.6H_2O$ in H_2SO_4, stored in nitrogen atmosphere and periodically standardised[7], was added from a semi-microburette. For titrations in hydrochloric acid and phosphoric acid, the titrant solutions were: $FeCl_2$ in HCl and $Fe(H_2PO_4)_2$ in H_3PO_4, the two ferrous salts being prepared by dissolving pure iron wire in hydrochloric acid[8] and phosphoric acid[9] respectively. Reagents used were all of AnalaR grade.

Differential titration curves were obtained by plotting the differential potential, E_Δ, against the volume of titrant (expressed as moles of Fe^{2+} per mole IO_3^-) added. In plotting each successive curve the titrant volume zero was progressively shifted along the X-axis but the same voltage scale was used for all the curves. Titrations were carried out mostly at room temperature (ca. 25°) but in sulphuric and phosphoric acid of moderate concentrations (below 10 N), the solutions titrated were heated to 60°, for obtaining smooth and reproducible titration curves and for rendering the electrode reactions more reversible. The shape and form of the curves was found also to depend both on the concentration of the acid solution and on the magnitude of the current density on the electrodes. Optimum conditions were established by performing titrations under varying conditions. In hydrochloric acid solutions sharp and reproducible peaks were obtained when the electrolysis current was 1μA to 2μA, the size of the wire electrodes were as long as 4.5cm and their distance apart also was 4.5cm. In sulphuric and phosphoric

acid solutions the electrolysis current density on the *indicator electrodes were much higher : the electrolysis* current being 5μA, the length of the wire electrodes 5mm which were 1.5cm apart.

Results

(i) *Titrations in hydrochloric acid solutions*: Titrations were performed in hydrochloric acid solutions of concentrations varying from 9N to 1N-typical titration curves [(A)2*N* HCl, (B)5*N* HCl, (C)7*N* HCl] are given in Figure 1. A single sharp peak in the differential curve is obtained in each case at exactly 2 moles of Fe^{2+} per mole IO_3^- provided the acid concentrations is below 6N. At higher acid concentrations the peak requires more than 2 moles Fe^{2+}, e. g. in (C) the peak is at 2.4 moles.

(ii) *Titrations in sulphuric acid solutions*: In these titrations sulphuric acid concentration was varied from 2*N* to 16N. Figure 2 contains some [(A)4NH_2SO_4, (B)10*N* H_2SO_4, (C)16*N* H_2SO_4] of the typical titration curves. Two sharp and reproducible peaks, a small one succeeded by a larger one, is obtained in each of the differential curves : at 2 moles and 5 moles of Fe^{2+} per mole IO_3^- respectively. Some of these titrations were repeated in presence of chloride ions, which resulted in the appearance of an additional peak [e.g. Figures 4: (A)6*N* H_2SO_4 and 0.04*M* KCl] at 4 moles of Fe^{2+} per mole of IO_3^-.

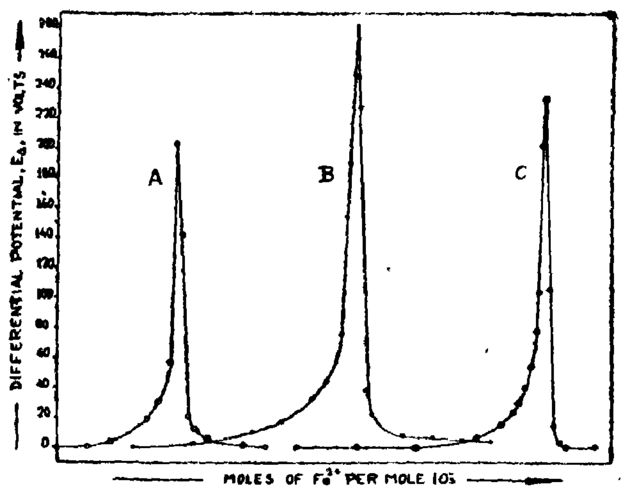


Fig. 1

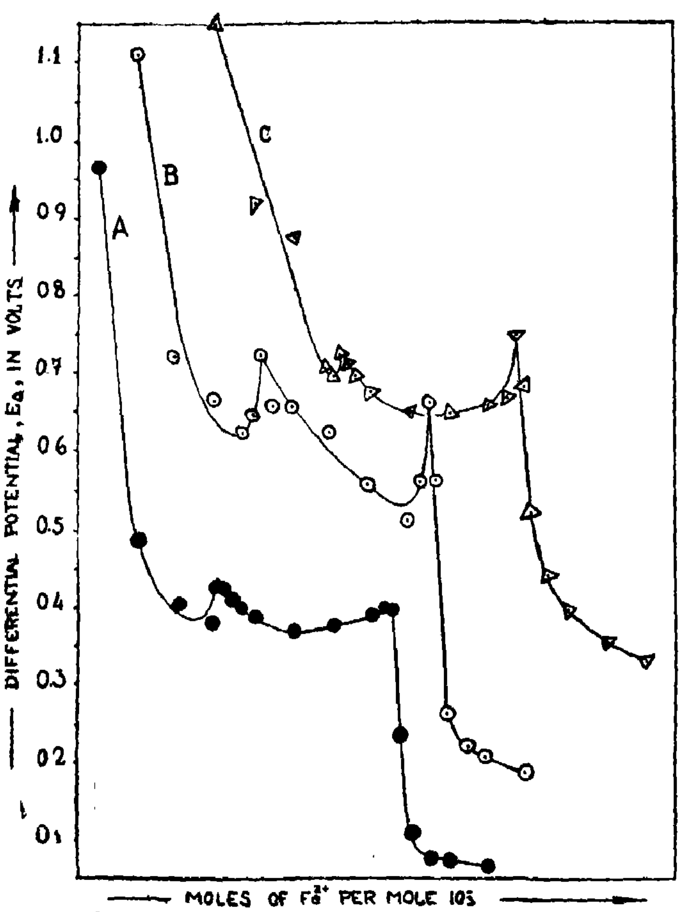


Fig. 2

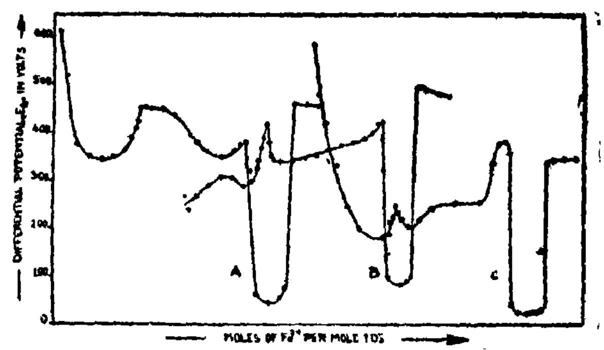


Fig. 3

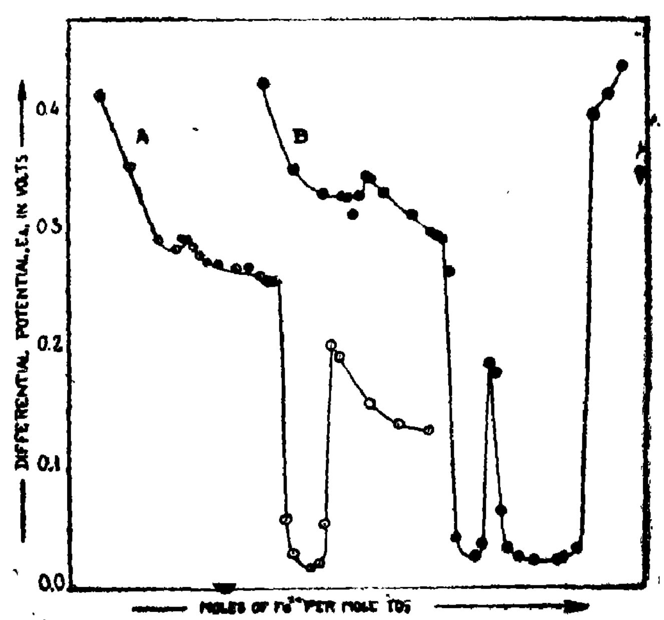


Fig. 4

(iii) *Titrations in phosphoric acid solutions*: Figure 3 contains some of the typical curves of titrations in presence of phosphoric acid [(A)4N H_3PO_4, (B)8N H_3PO_4, (C)14N H_3PO_4] of concentrations varying from 2N to 20N. An initial small peak at 2moles of Fe^{2+} is succeeded in each case by a larger one at 5moles of Fe^{2+} per mole IO_3^-. Beyond the second peak there is a vertical fall in the differential curve which then rises steeply showing a break (at about 6 moles in 14N H_3PO_4). This last break tends to disappear with H_3PO_4 concentration increasing beyond 14N, when the nature of the curves also change. Thus in 16N H_3PO_4 solution there is only one peak at 5moles of Fe^{2+} which is not very sharp. In presence of chloride ions an additional peak [e.g. figure 4 (B)6N H_3PO_4 and 0.1M KCl] at 4moles of Fe^{2+} per mole IO_3^- appears.

(iv) *Forms of titration curves*: Titrations in hydrochloric acid solutions yield symmetrical differential curves with sharp positive going peaks showing steep rise and fall (peak height 200mV) from near zero bases. In sulphuric acid solutions an initial fall in the differential curve is followed by a small but well defined peak. This is succeeded by a second peak larger than the first, beyond which the curve registers a steep vertical fall of about 400mV. In presence of potassium chloride the form of the curves is changed, and an additional peak appears in between the two peaks beyond which the curve falls steeply and then rises again—after which the final peak appears as before.

Initial portions of titration curves of titrations performed in phosphoric acid solutions resemble those from sulphuric acid solutions. The steeply falling portion of the curves beyond the second peak (peak height about 350mV), however, starts rising again and finally exhibits a break after which it tends to become flat. When chloride ion is present, the differential curve shows an additional break in between the two initial peaks.

Discussion

In hydrochloric acid solutions of concentrations between 2N to 6N the single peak in the differential curve at 2 moles of Fe^{2+} per mole of IO_3^- corresponds with the reduction of IO_3^- com pletely to ICl_3:

$$IO_3^- + 3Cl^- + 6H^+ + 2Fe^{2+} = ICl_3 + 3H_2O + 2Fe^{3+} \quad (1).$$

The reduction process does not seem to proceed further under the conditions in which the titrations are performed. Peaks requiring more than 2 moles Fe^{2+} at higher acid concentrations perhaps indicate partial reduction of ICl_3 to ICl or I_2. Iodine trichloride had been isolated and its thermodynamic properties have been measured.[10] Its formation during the reduction of IO_3^- in hydrochloric acid solutions has previously been noted[4]. Equation (1) involving formation of ICl_3, accords well with stoichiometric requirement of the titration curves but the formation of ICl_3 in preference to ICl is still to be explained.

Both in sulphuric and phosphoric acid solutions (concentrations between 4N to 16N) two peaks at 2 moles and 5 moles of Fe^{2+} per mole of IO_3^- corresponds with stepwise reduction of IO_3^-, first to I^{3+} and then finally to I_2. Thus in sulphuric acid the reduction of iodate to iodine may involve intermediate formation of iodine sulphate:

$$IO_3^- + \frac{3}{2}SO_4^{2-} + 6H^+ + 2Fe^{2+} = \frac{1}{2}I_2(SO_4)_3 + 3H_2O + 2Fe^{3+} \quad (2)$$

$$\frac{1}{2}I_2(SO_4)_3 + 3Fe^{2+} = \frac{1}{2}I_2 + \frac{3}{2}SO_4^{2-} + 3Fe^{3+} \quad (3)$$

Similarly in phosphoric acid solutions intermediate formation of iodine phosphate is indicated:

$$IO_3 + PO_4^{3-} + 6H^+ + 2Fe^{2+} = IPO_4 + 3H_2O + 2Fe^{3+} \quad (4)$$

$$IPO_4 + 3Fe^{2+} = \frac{1}{2}I_2 + PO_4^{3-} + 3Fe^{3+} \quad (5)$$

At the second peak at 5 moles of Fe^{2+} therefore the net reaction in both acids amount to:

$$IO_3^- + 6H^+ + 5Fe^{2+} = \frac{1}{2}I_2 + 3H_2O + 5Fe^{3+} \quad (6)$$

Equations (3) and (4) involve SO_4^{2-} and PO_4^{3-} ions which in high acid concentrations would not perhaps exist in appreciable amounts. These equations therefore may be considered to represent the overall reaction corresponding to stoichiometric requirements. In this context it may be mentioned that oxidation of iodine leads to the formation of salt like compounds of tripositive iodine,[11,12] including the sulphate $I_2(SO_4)_3$, and the phosphate, IPO_4. The assumption therefore of intermediate formation of these compounds during the reduction of iodate (initially formed I_2 being oxidized by IO_3^-) seems justified.

An interesting feature of titrations in these two acids in presence of chloride ions is the appearance of an additional peak at 4 moles of Fe^{2+} per mole IO_3^- which could correspond to initial reduction in presence of Cl^-, either of $I_2(SO_4)_3$ of IPO_4 to ICl.

$$\frac{1}{2}I_2(SO_4)_3 + 2Fe^{2+} + Cl^- = ICl + \frac{3}{2}SO_4^{2-} + 2Fe^{3+} \quad (7)$$

$$IPO_4 + Cl^- + 2Fe^{2+} = ICl + PO_4^{3-} + 2Fe^{3+} \quad (8)$$

Reduction of IO_3^- to ICl in strong HCl solutions was noted by Andrews[13]. However, we failed to get a peak corresponding to its formation in titrations in HCl solutions. In strong H_2SO_4 and H_3PO_4 on the other hand a relatively small concentration of Cl^- seems to lead to its formation according to the following net reaction:

$$IO_3^- + Cl^- + 6H^+ + 4Fe^{2+} = ICl + 3H_2O + 4Fe^{3+} \quad (9)$$

Another salient feature is that titration in phosphoric acid solutions yield curves with a further peak at about 6 moles of Fe^{2+} per mole of IO_3^-. It is possible that, in presence of PO_4^{3-} ions, iodine is further reduced by Fe^{2+} to I^- – this would correspond with :

$$\frac{1}{2}I_2+Fe^{2+}=I^-+Fe^{3+} \quad (10)$$

The overall reaction therefore would be

$$IO_3^-+6H^++6Fe^{2+}=I^-+3H_2O+6Fe^{3+} \quad (11)$$

It may be noted in this context that Bonner and Romeyn[14] have shown that the reaction (10) goes to completion in the presence of phosphate (even though the reaction is slow), probably due to the formation of a weak electrolyte of composition varying from $FePO_4$ to $Fe(H_2PO_4)_3$. The peak corresponding o reaction (10) is not reproducible probably because the reaction is slow.

Forms of differential curves throw some light on the reversibility of the species being electrolysed at the two polarised electrodes[2,6]. As steep rise and fall would indicate the existence of reversibly electrolysable species, we conclude from an examination of titration curves in Figures 1 to 4 that the tirant systems (i. e., Fe^{2+}/Fe^{3+} system) is reversible in HCl and H_2SO_4 solutions but is only partly reversible in phosphoric acid solutions. The titrate system, IO_3^-/I^{3+}, appears to be reversible in hydrochloric acid but only partly reversible in sulphuric acid and phosphoric acid solutions. The nature of the other relevant peaks would also suggest that the various systems involved in the reduction process (comprising I^{3+}, I^+, I^0 and I^-), are none of them wholly reversible.

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Molecular Adsorption and Ion-Exchange of Carboxylic Acids by Anion-Exchange Resin

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Molecular adsorption and ion-exchange of the carboxylic fatty acids (formic to n-butyric) by the anion-exchange resin, Amberlite-IRA-400, in its chloride and bromide forms, have been investigated. The adsorption increases in the order, formic < acetic < propionic < n-butyric. The order of ion-exchange by the two forms of the resin is found to be: Cl-resin: propionic < acetic < n-butyric < formic. Br-resin: acetic < propionic < n-butyric < formic. It is found that both adsorption and ion-exchange of the four acids are always greater with the chloride form than with the bromide form of the resin.

CARBOXYLIC fatty acids undergo molecular adsorption and ion-exchange simultaneously, when their solutions are equilibrated with the resin containing counter-ions different from that present in the resin. In the case of cation-exchange resin, H^+ ion of the weak organic acid is exchanged with the counter-ion of the resin. In anion-exchange resin, carboxylate ion of the acid is exchanged for the counter-ion different from the carboxylate ion. Devydov and Lisovina[1], while working with organic fatty acids, obtained "super adsorption" of these acids by weak-base anion-exchange resins. They did not differentiate between molecular adsorption and ion-exchange. Starobinets and Gleim[2], for the first time, differentiated between molecular adsorption and ion-exchange of weak organic acids (C_1 to C_9) by an anion-exchange resin. Ermolenko and Sviridova[3] obtained both molecular adsorption and ion-exchange of fumaric and maleic acids by anion-exchange resins.

In this paper, the results of a study on simultaneous molecular adsorption and ion-exchange properties of weak organic acids (formic to n-butyric) by an anion-exchange resin, Amberlite-IRA-400, in its chloride and bromide forms, are presented.

Experimental

Commercially obtained monofunctional highly basic anion-exchange resin, Amberlite-IRA-400, in chloride form was first converted to hydroxyl form by treating the resin with 0.5 *N* sodium hydroxide solution. The OH-resin was washed thoroughly with double distilled water to remove Cl^- and Na^+ ions and other ions which were originally present in the resin.

The OH-resin was then converted to chloride and bromide forms on repeated treatment with about *IN* HCl and *IN* KBr solutions respectively. The chloride and bromide resins, thus obtained, were washed with double distilled water to remove excess HCl and KBr. The washed resins were then dried in air and kept in a closed container.

Formic, acetic, propionic and n-butyric acids were of purely "Analar grades" and so used without further purification.

The total exchange capacity of the resin was 2.52 ± 0.02 meq/gm. dry resin. Weighed amounts (about 1 gm) of the resin of known moisture content were taken in well stoppered Jena glass bottles. These were then shaken with acid solutions (50 ml each) of known concentrations by a mechanical shaker for 4 hours. After attainment of equilibrium, the equilibrium concentrations of the acids and Cl^- or Br^- ion in the solutions were estimated by means of suitable analytical methods.

The initial and final concentrations of the acids were found out by alkalimetric titration. The concentrations of chloride and bromide ions were estimated in separate aliquots by titrating with standard silver nitrate solution using fluorescein adsorption indicator[4]. From the concentrations of chloride and bromide ions, ion-exchanges of these ions were calculated. The molecular adsorption of the acid was calculated from the difference between initial and final concentration of the acid.

* Senior author

All the experiments were done in room temperatures (30±2°).

Results and Discussions

Molecular adsorption and ion-exchange isotherms of carboxylic acids on the chloride and bromide forms are presented graphically in figures 1a, 1b, 2a and 2b respectively. Both adsorption and ion-exchange increase with equilibrium concentrations of the acids. As expected, the adsorption is found to be increased with the chainlength of the carboxylic acids. The order of ion-exchange by the two salt forms of the resin is,

Cl-resin : propionic $<$ acetic $<$ n-butyric $<$ formic.
Br-resin : acetic $<$ propionic $<$ n-butyric $<$ formic.

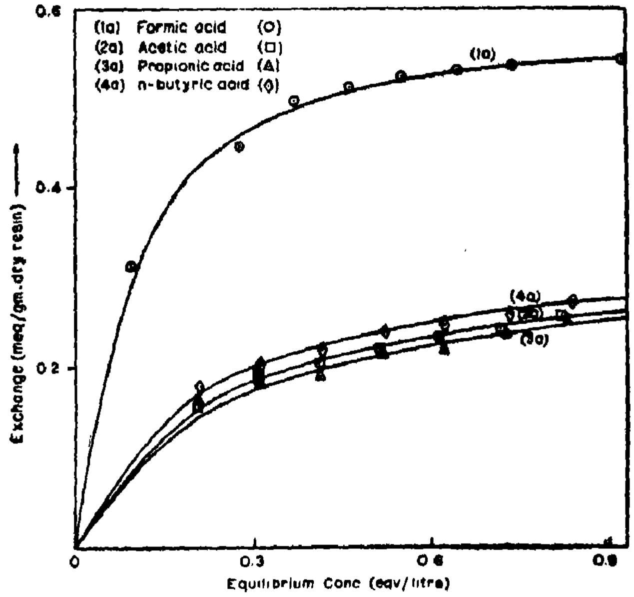


Fig. 1.a) Exchange Isotherms of Carboxylic acids on the Chloride form of Amberlite-IRA-400.

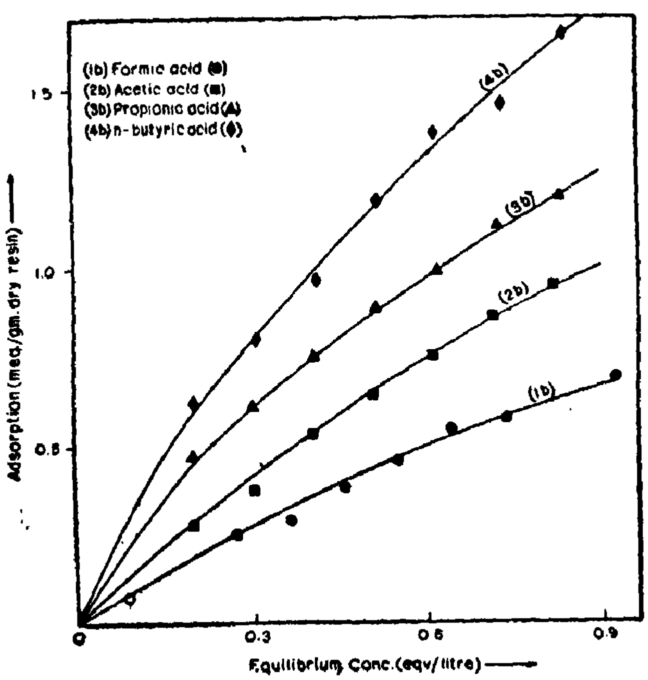


Fig. 1.b) Adsorption isotherms of Carboxylic acids on the Chloride form of Amberlite-IRA-400.

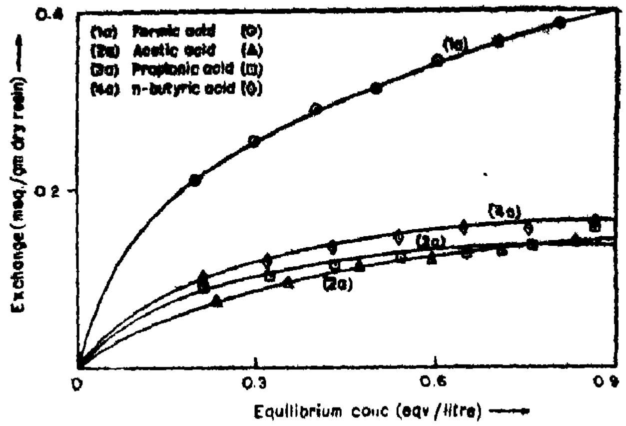


Fig. 2.a) Exchange Isotherms of Carboxylic acids on the Bromide form of Amberlite-IRA-400.

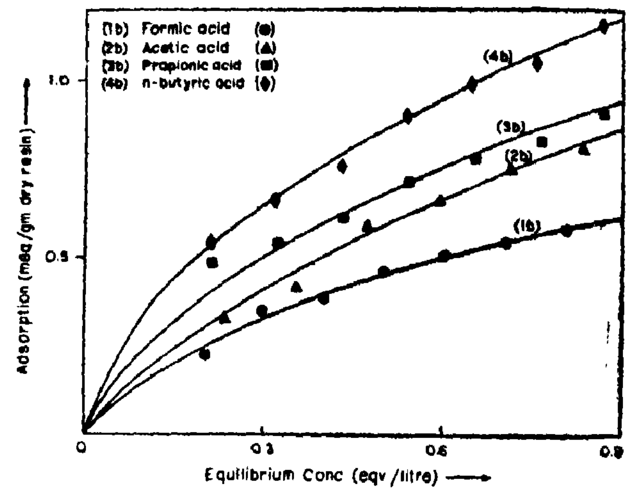


Fig. 2.b) Adsorption Isotherms of Carboxylic acids on the Bromide form of Amberlite-IRA-400.

Formic acid has the largest dissociation constant among the all four carboxylic acids studied and so the ion-exchange with this acid is also highest. But with the other acids, not only the dissociation constant but also the chainlength play an important part in ion-exchange. The increasing chainlength increases the hydrophobic nature of the carboxylate ions and consequently the increase in selectivity for these ions is due to the hydrophobic interactions with the resin[5,6].

It is observed that for all the four carboxylic acids ion-exchange is always greater with the chloride form of the resin than with the bromide form. Similar is the case with molecular adsorption. As the selectivity of Br^- ion is more than Cl^- ion by the anion-exchange resin, the molecular adsorption as well as ion-exchage is smaller in bromide form than in chloride form of the resin. Starobinets and Gleim[2] showed that stronger is the electrostatic interaction between the ion fixed and the opposite ion, the weaker is the carboxylate groups attracted by the resin matrix and consequently the

molecular adsorption is smaller. But the effect of electrostatic interaction on the molecular adsorption is not always the main factor. If we compare the molecular adsorption of a particular acid by all the salt forms of the anion-exchange resin, presented here and in our previous paper[7], following results can be obtained.

Acids	*Adsorption*
Formic :	$RNO_3 < RCl = RBr < HCOOR < R_2SO_4 < R_2CrO_4$.
Acetic :	$RBr < RCl < RNO_3 < CH_3COOR = R_2SO_4 < R_2CrO_4$.
Propionic :	$RBr < RCl < RNO_3 < CH_3CH_2COOR = R_2SO_4 < R_2CrO_4$.
n-butyric :	$RBr < RCl < RNO_3 < R_2SO_4 < CH_3CH_2CH_2COOR < R_2CrO_4$.

R = Resin matrix.

The order of the selectivity of the anions for the anion-exchange resin is[8],

$$Cl^- < Br^- < NO_3^- < \text{carboxylate} < CrO_4^{2-} < SO_4^{2-}.$$

From the selectivity order, it is found that SO_4^{2-} ion has the largest selectivity among other ions given here. It has already been mentioned in our previous communications[7] that due to site sharing[8] acids are adsorbed strongly by the sulphate and chromate forms of the resin.

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Ion-Solvent Interaction in Mixed Solvents : Viscosity of Bromates, Iodates and Sulphates of Potassium and Sodium in Dioxane-Water Mixtures at Different Temperatures

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The viscosities of the bromates, iodates and sulphates of potassium and sodium at 10, 20 and 30% dioxane-water mixtures (by wt.) have been measured at 30, 35, 40 and 45°. The data have been analysed in terms of Jones-Dole equation :

$$\eta_r = 1 + AC^{1/2} + BC$$

The values of the constants A and B indicate ion-ion and ion-solvent interaction respectively, and ion-ion interaction is of the order $SO_4^{--} > IO_3^- > BrO_3^-$ and ion-solvent interaction order is $BrO_3^- > IO_3^- > SO_4^{--}$.

THE viscosity measurements of $KBrO_3$, $NaBrO_3$, KIO_3, $NaIO_3$, K_2SO_4 and Na_2SO_4 in dioxane-water mixtures (by wt.) have been carried out at 30,35, 40 and 45±0 01°. The data have been interpreted in terms of the Jones-Dole equation[1] :

$$\eta_r = 1 + AC^{1/2} + BC \quad (1)$$

where η_r is the relative viscosity of the solution, C is the concentration of the electrolyte and A and B are constants. The coefficient A is due to the contribution from interionic electrostatic forces[2-4], and B gives the measure of the order or disorder introduced by the ions into the solvent structure.

A review of the literature shows that no general theory has yet been developed for B-coefficient, however, it is a manifestation of ion-solvent interaction[5]. In the present investigation, interest, therefore, centres on the coefficient of B. The nature of the B coefficient as pointed out by Cox and Wolfenden[6] is attributed to its specific additive character depending on the constituent ions. On the other hand Asmus[7] used the entropy of hydration to correlate ionic B values and recently a single linear relationship between the ionic B values and molar entropy of hydration has been obtained by Nightingale[8].

Experimental

The salts $KBrO_3$, $NaBrO_3$, KIO_3, $NaBrO_3$, K_2SO_4 and Na_2SO_4 used were of E. Merck 'extra pure' variety. The SO_4^{--} contents were estimated in the usual manner[9]. The preparation of solvents, and solutions were the same as described earlier[10]. The viscometric technique were the same as that of Chackravarty and Prasad[11]. The densities of the solutions and the solvents were determined by pycnometer (50 cc. capacity) with buoyancy correction and is same as that of Srinivasan & Prasad[12]. All sorts of precautions were taken to check the evaporation of the solvent[13]. The time flow differs by 0.2 secs in 20 minutes and have an error of ±0.04%. Density readings were precise upto ±0.0002 gm/ml. i. e. an error upto 4 in 10^6. The concentration range was from 0.1*M* to 0.001*M*.

Results & Discussion

Viscosities of the mixed solvents as well as those containing salts solutions under study were measured. The results have been analysed in terms of Jones-Dole equation[1] as the plot of $(\eta_r - 1)/C^{1/2}$ vs $C^{1/2}$ is linear. The intercept and the slope of the plot give respectively the coefficients of A and B. The coefficient A and B thus obtained for various salts are given in Table-1 and 2 respectively. The calculated values of A[14] are in good agreement with those of the observed one. The relative viscosities calculated from these values of A and B, are found to be in acceptable agreement with the experimental values.

A Values :

The different 'A' values (Table-1) of all the six salts studied indicate dependence of ionic interactions on the nature of the electrolyte and are all positive. The electrostatic ion-ion interaction and hence the value of 'A' is found to increase with the decrease in the dielectric constaht of the medium when the concentration of the dioxane increases in the mixture. From

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TABLE 1

$A \times 10^3$ values in $1^{1/2}$ mol. $^{-1/2}$

Temp.°C	10%D	20%D	30%D	10%D	20%D	30%
		$KBrO_3$			$NaBrO_3$	
30	6.9	7.1	8.2	7.2	7.4	8.9
35	6.2	6.6	7.9	6.3	7.0	8.2
40	5.8	6.0	7.4	5.9	6.2	7.4
45	5.4	5.8	6.9	5.5	5.9	6.3
		KIO_3			$NaIO_3$	
30	7.2	8.1	9.6	7.8	8.7	10.2
35	6.7	7.3	8.9	7.5	8.4	9.7
40	6.0	6.8	8.0	7.8	7.9	9.1
45	5.4	6.0	7.2	6.6	7.2	8.4
		K_2SO_4			Na_2SO_4	
30	13.5	16.0	26.6	13.9	16.6	17.2
35	13.0	15.0	26.0	13.4	15.2	16.0
40	12.2	14.2	24.2	12.6	14.1	14.6
45	11.6	12.6	22.2	12.1	13.4	13.9

table-1, it is seen that the ion-ion interaction is of the order : $SO_4^{--} > IO_3^- > BrO_3^-$. Further, the value of 'A' decreases with the rise of temperature for all the salts which one should expect in view of more thermal agitation at higher temperatures and reduction of attractive forces.

Dependence of B on temperature :

According to Stokes and Mills[15] the viscosity of a dilute electrolytic solution incorporate that of solvent plus the contribution from other sources. They are, η^E, the positive increase due to the shape and size of an ion ; η^A, the increase due to the alignment on orientation of the polar molecules by the ionic field and η^D, the decrease in the viscosity arising due to the distortion of the solvent structure by the ions. Therefore, B-coefficient can be discussed in terms of these viscosity effects at different temperatures.

The B-coefficient of all the six salts increases with the increase in temperature. This indicates that the viscosity decrease due to solvent structure, i. e. η^D is small and hence $\eta^E + \eta^A > \eta^D$ and 'B' is positive. The 'B' value is found to be of the order : $SO_4^{--} > IO_3^- > BrO_3^-$. Hence, it can be concluded that distortion of solvent structures or ion-solvent interaction is of the reverse order, i. e. $BrO_3^- > IO_3^- > SO_4^{--}$.

Further according to Stokes & Mills[15], the lesser the value of dB/dt, the greater is the ion-solvent interaction. In the present case the plot of 'B' vs 't' is linear and the slope dB/dt is found to be of the order, $SO_4^{--} > IO_3^- > BrO_3^-$. This indicates that the ion-solvent interaction is of the order $BrO_3^- > IO_3^- > SO_4^{--}$, which confirms the above interpretation.

Dependence of 'B' on cation :

Ions with greater crystal radii and small surface change density, K^+, would have a weak orienting effect in the first layer. Therefore, η^E and η^A will be small. Also there exists a considerable amount of distortion in the vicinity of such ions due to the competition between the ionic field and bulk structure and consequently η^D will be large. Thus 'B' will be smaller for K^+ salts than for Na^+ salts (Table-2). So the order of ion-solvent interaction is $K^+ > Na^+$.

Dependence of 'B' dioxane content :

McRae[16] has suggested that the dioxane molecule has two non adjacent dipolar groups whose moment cancel, so that the effective reaction field is probably greater than is indicated by microscopic properties. Hence, the frozen layers, as suggested by Frank and Evans[17], around the cation be expected to be constituted of both the water molecules and the dioxane molecules possibly consisting more of the former than the

TABLE 2

B values in lit. mol⁻¹

Temp. °C	10% D	20% D	30% D	10%	20% D	30% D
		$KBrO_3$			$NaBrO_3$	
30	0.0300	0.042	0.062	.065	0.089	0.104
35	0.043	0.059	0.078	0.089	0.109	0.119
40	0.058	0.076	0.098	0.104	0.122	0.134
45	0.074	0.092	0.114	0.122	0.138	0.146
		KIO_3			$NaIO_3$	
30	0.120	0.145	0.165	0.181	0.212	0.252
35	0.152	0.164	0.175	0.210	0.235	0.264
40	0.165	0.185	0.220	0.235	0.255	0.281
45	0.185	0.205	0.245	0.263	0.278	0.295
		K_2SO_4			Na_2SO_4	
30	0.248	0.275	0.348	0.262	0.291	0.385
35	0.280	0.300	0.380	0.300	0.325	0.410
40	0.305	0.330	0.415	0.330	0.352	0.438
45	0.330	0.388	0.434	0.360	0.378	0.448

latter kind of molecules ; whereas, the diffused layer would consist of loosely oriented water and dioxane molecules, the extent of orientation decreasing with the distance from the ion till the outermost layer has the same structure and composition as that of the solvent. When the dioxane content of the solvent increases, more dioxane molecules take part in constituting the diffused layer and thus promoting a sort of ordering effect in the solvation sphere and hence would lead to larger values of η^E and η^A and exibit an increase in the value of 'B' with increase in dioxane content (Table-2).

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Calculation of b* of Laidler and Landskroener Equation for General Ion-Dipole Type of Reactions in Solutions and its Application

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The Laidler and Landskroener method for evaluating b*, the distance of closest approach of solvent molecules to the activated complex in a bimolecular reaction is applicable only when the transition state is highly polarized. A more general method for calculating b* in case of above mentioned reactions, irrespective of the polarity of the transition state and free from any assumptions about the model of the activated complex, has been suggested. The method has been applied in alkaline hydrolysis of ethylacetate in water enriched DMSO between 30 and 35°. The b* was found to be 2.41 A° which is in agreement with the value obtained from the data of D. D. Roberts.

AMONG the various theoretical expressions, relating rate constant with the properties of solvents and reactants, the Laidler and Landskroener equation[1] is most widely accepted. The equation for ion-dipole type of bimolecular reaction in solutions in which the transition state is much more polarized than the initial state, can be expressed as follows ;

$$\log k = \log k_0 + \frac{1}{2.303}\frac{e^2}{2kT}\left(\frac{1}{b_A}-\frac{1}{b^*}-\frac{3G^*}{2b^{*3}}\right)\frac{1}{D} + \frac{1}{2.303}\frac{e^2}{2kT}\left(\frac{1}{b^*}-\frac{1}{b_A}+\frac{3G^*}{4b^{*3}}\right) \quad (1)$$

The applicability of the above equation has been tested by Laidler and Landskroener themselves by calculating the value of b* for several ion-dipole type of bimolecular reactions yielding a negative slope for log k against $\frac{1}{D}$. The method of computation of b* as well as G* has been refined and simplified by proposing a pair of equations by the authors of these lines in their previous communication[2]. However, the computation suffers from an arbitrary assumption about the dielectric constant of ideal solution and the equations have not been applied for those ion-dipole type of reactions in which a linear relationship of log k against $\frac{1}{D}$ yields a positive slope. Therefore the present work is undertaken with a view (i) to propose an equation for the variation of specific rate constant for an ion-dipole type of bimolecular reactions in which the transition state may or may not be polarized and the slope of log k against $\frac{1}{D}$ may be positive or negative, (ii) to develop a new method for computation of b*, the distance of closest approach of solvent molecules to the transition state, in which no assumption about the dielectric constant of ideal solution is needed, and (iii) to test the applicability of the proposed equation in cases where a plot of log k against $\frac{1}{D}$ results in a straight line with positive slope.

With increasing researches on solvent effect it is now clearly recognised that the action of non-aqueous component of a mixture is more than simple diluent or modifier of its dielectric properties. Recently, it has been reported[3] that DMSO as a cosolvent of water leads to a breakdown of water-water interactions forming an intermolecular association with it. Wolford[4] on the basis of kinetic studies in DMSO-water mixtures concluded that the mixtures can be divided into three regions, molefraction of DMSO varying from 0 – 0.3, 0.3 – 0.45 and 0.45 – 1.0. Prior to above reporting D. D. Roberts[5,6] studied the alkaline hydrolysis of ethylacetate in DMSO-water mixture in the Wolford's second region of the mixture, obtaining a positive slope for the variation of log k against $\frac{1}{D}$. Therefore the authors selected to study the same reaction but in the first region of DMSO-water mixture in order to explore the pronounced specific effects of the solvent mixture if any and to apply the data thus obtained in the evaluation of b* of Laidler-Landskroener equation. It would seem to the authors that in this region the size of the ions would be nearly of the same dimension as in water alone.

Experimental

Standard solutions of NaOH (0.05 *M*) and ethylacetate (0.033*M*) were prepared in solvent mixture of A. R. grade DMSO varying from 5-25% in double distilled water. The above solutions in a particular solvent composition were thermostated in a bath controlled within ±0.5°. After mixing equal volume of both the solutions, the kinetics of the reaction were followed by removing 10 ml of liquid from the reaction mixture at different intervals of time and adding it to a

known excess of standard ice cold HCl solution, the excess of which was estimated with standard baryta solution. Reproducible results were always obtained. The specific rate calculated in various solvent mixtures at 30.2° and 35° are shown in table 1. The table also includes the dielectric constant values extrapolated from the curve using the data of Wolford[4]. Akerlof's equation[7] was used for changing the values to different temperatures.

TABLE 1—SPECIFIC RATE CONSTANTS IN WATER—DMSO MIXTURES

Solvent composition % (v/v) of DMSO	K, specific rate constant at		Dielectric constants of solvent mixtures at	
	30.2°C	35°C	30.2°C	35°C
5	7.17	11.15	76.43	74.73
10	7.58	12.01	76.33	74.63
15	7.95	12.46	76.17	74.50
20	8.52	12.68	76.00	74.30
25	9.04	13.76	75.80	74.05

Discussion

The Laidler-Landskroener equation is based on the assumption that the change in the solvent composition results in the change of activity coefficient. The activity coefficient expression for Zwitter ions in a solution has been given by Kirkwood [8,9] which may be expressed as follows, if the dielectric constant of the solute is taken into account.

$$\ln\gamma = \frac{e^2}{2kT}\left[\frac{1}{D}\left\{\frac{Z^2}{b}+\frac{3G}{2b^3}\right\}-\left\{\frac{Z^2}{b}+\frac{3G}{2(1+\alpha)b^3}\right\}\right] \qquad (2)$$

where, G is a number depending on the distribution of charges and proportional to dipole moment and α is half of the dielectric constant of solute. The other terms have their usual significance.

For a bimolecular reaction of type

$$A+B \rightarrow AB^*$$

in solution, rate coefficient is expressed as

$$\ln k = \ln k_0 + \ln\frac{\gamma A\gamma B}{\gamma AB^*}$$

Similarly, using equation (2) for an ion-dipole type of bimolecular reaction, following the method of Laidler and Landskroener, one can express :

$$\lg k = \log k_0 + \frac{1}{2.303}\,\frac{e^2}{2kT}\left[\left\{\left(\frac{1}{b_A}-\frac{1}{b^*}+\frac{3}{2}\sum\frac{G}{b^3}\right)\frac{1}{D}\right\} - \left\{\frac{1}{b_A}-\frac{1}{b^*}+\frac{3}{2(1+\alpha)}\sum\frac{G}{b^3}\right\}\right] \qquad (3)$$

where $\sum\frac{G}{b^3}=\left(\frac{G_A}{b_A3}+\frac{G_B}{b_B3}-\frac{G^*}{b^{*3}}\right)$

and it is proportional to the change in the polarization of the reactants due to formation of the transition state. Expressing equation (3) in a more general form,

$$\log k = \log k_0 + \frac{X}{TD}+\frac{Y}{T} \qquad (4)$$

where $X=\frac{1}{2.303}\,\frac{e^2}{2k}\left(\frac{1}{b_A}-\frac{1}{b^*}+\frac{3}{2}\sum\frac{G}{b^3}\right)$

and $Y=-\frac{1}{2.303}\,\frac{e^2}{2k},\left(\frac{1}{b_A}-\frac{1}{b^*}+\frac{3}{2(1+\alpha)}\sum\frac{G}{b^3}\right)$

Rearranging the expressions for X and Y and putting

$A=\frac{1}{2.303}\,\frac{e^2}{2k}$, we get

$$\frac{1}{b_A}-\frac{1}{b^*}+\frac{3}{2}\sum\frac{G}{b^3}=\frac{X}{A} \qquad (5)$$

and
$$\frac{1}{b_A}-\frac{1}{b^*}+\frac{3}{2(1+\alpha)}\sum\frac{G}{b^3}=-\frac{Y}{A} \qquad (6)$$

subtracting equation (6) from (5)

$$\frac{3\alpha}{2(1+\alpha)}\sum\frac{G}{b^3}=\frac{X+Y}{A} \qquad (7)$$

substituting the value $\sum\frac{G}{b^3}$ in equation (5) the desired expression is obtained as follows :

$$\frac{1}{b_A}-\frac{1}{b^*}=\frac{1}{A}\left[X-\frac{1+\alpha}{\alpha}\left(X+Y\right)\right] \qquad (8)$$

The value of X can be obtained from the slope of log k against $\frac{1}{D}$ and the mean value of Y between two temperatures close to the experimental temperature can be determined from the expression,

$$\log\frac{k_1}{k_2}=\left(\frac{X_1}{D_1T_1}-\frac{X_2}{D_2T_2}\right)+Y\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \qquad (9)$$

the terms with subscript 1 and 2 represent their values at temperatures T_1 and T_2.

In case of alkaline hydrolysis of ethylacetate in water enriched DMSO, the graph of log k against $\frac{1}{D}$ was found to be linear and the value of $\frac{X}{T}$ at 30.2° and 35° calculated from the slope were 905.5 and 651.5 respectively. The values of Y between 30.2 and 35°

evaluated with the help of equation (9) are shown in table 2. The size of OH^- ion (b_A) in aqueous medium was calculated to be 3.69 A° from its molar volume[10] and the size of H_3O^+ ion in water.

TABLE 2—VALUES OF X, Y AND b* IN WATER-DMSO MIXTURES

Composition of solvent in %(v/v)	Values of Y	Value of $\frac{X}{T}$ at 30.2°C	b* in A° at 30.2°C
5	−64,710		2.41
10	−64,680		2.41
15	−64,860	905.5	2.45
20	−64,550		2.39
25	−64,680		2.41

Thus using the values of $\frac{X}{T}$, mean Y, and b_A the values of b* were calculated with the help of equation (8) at 30.2° as reported in table 2. The average value of b* comes to 2.415 A°. The value of b* was also calculated from the data of D. D. Roberts[6] using the equation (8) at 25°, which was found to be 2.02 A°. The b* value could not be calculated at 30.2° from the data of Roberts due to lack of sufficient data. However, the agreement with our value is quite good considering the difference in temperature and that of the solvent composition.

According to the Kirkwood theory[8,9] these radii should not correspond to the overall radii, but should be effective radii related to the size of the active groups in the complex molecules. Therefore the essential factor is the closeness of approach of the solvent molecules to the seat of reactions. It is quite possible that the solvent sheath over the OH^- ion present in the bulk is removed in the transition state and similar to the spreading of the charge, the solvent sheath too spreads over the transition state. Again, the solvation of the transition state will be much less in comparison to reactant ion due to the decrease in the charge density. As the size of the bare OH^- ion is 1.4 A° the effective size of the transition state species, defined as the distance of closest approach of a solvent molecule to the seat of reaction, found to be 2.415 A° is not unreasonable.

The distance of C–O bond reported[12] is of the order 1.43 A°. Therefore it is quite reasonable that the new C...OH^- bond which is being formed in the transition state due to the attack of OH^- ion on the carbonyl group of the ester may lie between 2 to 3 A° in case of simple ester hydrolysis. Thus the method proposed for evaluating b*, which is a very important parameter for predicting solvent effect, appears to be quite convincing. And as the method is more general and simple, its applicability is greatly increased. In ion dipole type of reactions with transition state less polarized or with reverse polarity the Laidler-Landskroener method can not be applied for calculating b*, where as the method suggested in the article can be applied satisfactorily to calculate b* even in those cases. However, further investegations are in progress to apply the method suggested in various types of ion-dipole reactions in solution in different solvent mixtures.

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Dipole Moments and I.R. Spectral Studies of the Complexes formed in the Mixtures of Phenylenediamine with Naphthols

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Dipole moments and I.R. spectral measurements of the complexes formed in the mixtures of *o*-phenylenediamine + α-naphthol, + β-naphthol, and *m*-phenylenediamine + α-naphthol have been made. The nature of complexes formed in these mixtures have been discussed.

SOLID+liquid phase diagrams indicated[1] the presence of 1/1 and 1/2 complexes in the mixtures of *o*-phenylenediamine + α-naphthol (1/1), *o*-phenylenediamine+β-naphthol (1/1), *m*-phenylenediamine + α-naphthol (1/1), *m*-phenylenediamine+β-naphthol (1/2), *p*-phenylenediamine + α-naphthol (1/2), and *p*-phenylenediamine + β-naphthol (1/2). In this paper we report the dipole moments of the 1/1 complexes formed in the first three mixtures and I.R. spectral measurements of all the complexes and the pure components. Dipole moment measurements may be related to hydrogen bonding[2], dipole association[3], association constants[4], interaction energy[5] and to the nature of forces[6] operating between the components of the mixtures. We restricted our measurements of dipole moment to 1/1 complexes as Weissberger method[7] of calculating induced moments may be applied to systems forming 1/1 complexes.

Experimental

o-, *m*-, and *p*-Phenylenediamines were fractionally crystallized from ethyl alcohol. α-, and β-Naphthols were fractionally crystallized from benzene. The purities of the samples were checked by thin layer chromatography and by determining the melting temperatures, which agreed to within ±0.1 K with the values reported in literature[8,9].

The complexes were prepared in molar ratios calculated from phase diagrams[1] by the method described earlier[10]. The dielectric constants of the complexes in benzene determined from the capacity measurements using Universal Impedance Bridge (type EE 01-02a, Toshniwal) at 308 15 K. The samples were placed in a cell containing a coaxial brass cylinder, the mouth of the cell was closed with a glass stopper to eliminate errors due to evaporation. The cell containing the sample was placed in a thermostat whose temperature was controlled to 0.1 K. the instrument was calibrated beforehand with several samples of pure liquids such as benzene, toluene, cyclohexane, chlorobenzene, carbon tetrachloride, *o*-xylene, and *m*-xylene. The values of dielectric constant for these compounds agreed to within 0.001 with the corresponding literature values[8,11]. The refractive indices were measured using an Abbe refractometer which was thermostated at 308.15 K by circulating water through it.

Specific volumes were measured from their density values. The densities were measured using a pyknometer designed for this purpose at 308.15 K in a thermostat. I.R. spectral measurements of the pure components and the complexes were made in chloroform with Specord 71-IR. I.R. spectra of pure components were taken at different dilutions.

Results

The dipole moments were calculated by the method of Richard and Walker[12]. The details are shown in Table 1.

The dissociation of the complexes in solution was studied from optical measurements by various methods[13-15]. Optical measurements were made in alcohol using filters of 546 and 436 nm (Erma Colorimeter) by the method described earlier[16]. The nature of the complexes in solution phase was found to be the same as in the solid phase. Plots of optical density against concentration were linear indicating that dissociation is very small and does not have any significant effect on dipole moment.

Discussion

The dipole moments in Table 1 have been collected (i) to determine the angle between the donor and acceptor molecules in the complex, and (ii) to study dipole interactions. As is evident from Table 1, μ_{comp} is greater than the sum of dipole moments of its components and so it is not feasible to determine the angle between the two interacting molecules. The main stumbling block seems to be the changes in the dipole moments of donor and acceptor molecules when they interact to form the complex. This interaction causes a

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TABLE 1—DIPOLE MOMENTS OF PURE COMPONENTS AND COMPLEXES

Substance	α	β	γ	μ/D	Δμ/D	Induced moment/D
o-phenylenediamine				1.46		
m-phenylenediamine				1.80		
α-naphthol				1.46		
β-naphthol				1.56		
xo-phenylenediamine+(1−x)α-naphthol	9.735	0.932	−0.489	3.531	0.61	0.2
xo-phenylenediamine+(1−x) β-naphthol	11.464	0.933	−0.165	3.76	0.75	0.2
xm-phenylenediamine+(1−x)α-naphthol	8.663	0.187	−0.379	3.32	0.06	0.2

polarization which changes dipole moments of the individual components by an unknown amount. Thus the change in dipole moment $\triangle\mu$, i.e., $\mu_{comp} -(\mu_1' + \mu_2) = \triangle\mu$, is either due to bond formation or due to induced dipole moments. The induced dipole moment in these complexes have been calculated by the method of Hampson and Weissberger[7]. The induced moments have been calculated by assuming the distance r to be 5 A° which is quite reasonable[17]. The induced moments of the 1/1 complexes thus calculated have been compared with the corresponding $\triangle\mu$ values in Table 1.

In the complexes of *m*-phenylenediamine+α-naphthol (Table 1), the major contribution to the value of $\triangle\mu$ is from induced moments, indicating that dipole-dipole forces are more prominent in this complex. In the complexes of *o*-phenylenediamine +α-naphthol, and +β-naphthol, it is evident that $\triangle\mu$ is not solely caused by dipole–dipole interactions or induced moments. The higher values of $\triangle\mu$ indicates that there is an appreciable increase of moment on complex formation. A part of change is probably due to induced moments and remaining due to hydrogen bond formation.

TABLE 2—I. R. ABSORPTION FREQUENCIES OF THE PURE COMPONENTS AND COMPLEXES

Substance	Hydrogen bond cm^{-1}	O-H bending cm^{-1}	O-H out of plane deformation/cm^{-1}
α-Naphthol	2930,3480	1350,1375	—
β-naphthol	3450	1370	
o-phenylenediamine	2920,3300	—	700-850
m-phenylenediamine	2920,3300	—	700-850
p-phenylenediamine	2920,3300	—	720-820
xo-phenylenediamine+(1−x) α-naphthol	2940,3300	1350,1380	700-850
xo-phenylenediamine+(1−x) β-naphthol	2940 3310,3480	1365,1380	700-820
xm-phenylenediamine+(1−x) α-naphthol	2960,3100-3200,3320	1310,1360	710-830
xm-phenylenediamine+(1−x) β-naphthol	2960,3100-3200,3320	1350,1370	710-840
xp-phenylenediamine+(1−x) α-naphthol	2900	1385	—
xp-phenylenediamine+(1−x) β-naphthol	2920,3300	1370	700-800

I.R. absorption frequencies for the pure components and the complexes are recorded in Table 2. The infrared absorption frequencies indicate the presence of hydrogen bonding in the 1/1 complexes and also in the 1/2 complexes formed in the mixtures of *m*-phenylenediamine + β-naphthol, *p*-phenylenediamine + α-naphthol, and *p*-phenylenediamine + β-naphthol.

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Semi-Empirical Potential Surfaces for Some Mixed Alkali Trimers

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Potential energy surfaces, binding energy and equilibrium geometry of some mixed alkali trimers have been calculated by a semi-empirical method based on London's equation. Calculated potential surfaces are shown in the form of contour maps. At small internuclear distances, these surfaces are characterised by shallow potential wells extending into the entrance and exit valleys without an energy barrier. The trimers are found to be stable over a range of linear and bent configurations, the most stable configuration in each case being a linear one with the lighter alkali atom occupying the central position. This configuration is also symmetric in all cases excepting NaLiLi.

THE exchange reactions of alkali atoms with alkali dimers ($M' + M_2 \rightarrow M'M + M$, where M and M' may be the same or different atoms) are believed[1] to proceed via alkali trimers as the stable intermediates. A knowledge of the potential energy surfaces of these trimers is of considerable importance in order to help resolve the reaction dynamics of such reactions. Although there is experimental evidence[2] indicating that the trimers of all alkalis are stable molecules, nothing is known experimentally about their binding energy and geometry. No sufficient theoretical work has also been done on these systems. Ab initio calculations of Davis and Del Conde[3] suggest that with respect to $Li+Li_2$, Li_3 is bound by 3Kcal/mole in its linear configuration and by about 10 Kcal/mole in its isosceles triangular configuration. Semiempirical diatomics-in-molecules[4,5] and valence bond[6,7] calculations show that the trimers of Li and Na (M_3 and $M'M_2$ types) are stable by 4-11 Kcal/mole and those of K, Rb and Cs (M_3 type) by 2-4 Kcal/mole with respect to atom-dimer dissociation. Recently, molecular beam reactive scattering has been measured[8] for the exchange reactions of Na with K_2, Rb_2 and Cs_2, and of K with Rb_2. However, neither experimental nor theoretical information are as yet available for the potential energy surfaces of these reactions. The present status of ab initio calculations[3] on alkali trimers seems to indicate that it is extremely difficult to apply these methods to the heavier trimers. It is, therefore, the purpose of the present investigation to calculate semiempirically these potential surfaces and to deduce therefrom the binding energy and geometry of the relevant trimers. In order to compare our results with those of some similar calculations[6]. potential energy surfaces of $Li+Na_2$ and $Na+Li_2$ have also been calculated.

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Results and Discussion

The method of calculation followed here is the same as given in details by Whitehead and Grice[6]. It makes use of the famous London equation[9]. The diatomic coulomb and exchange integrals occurring in this equation have been evaluated from the potential energy curves of the ground and triplet states of alkali dimers. The Morse[10] and Rydberg[11] potentials have been used for the ground state (both of these potentials have been used for the sake of comparison) and a modified anti-Morse potential proposed by us[12] has been used for the triplet state. Experimental values of the potential parameters needed to evaluate these potentials are taken from Herzberg[13]. In cases where experimental values are not available, use has been made of the results of split-shell MO calculations of Sannigrahi and Noor Mohammad[14].

The binding energy of the trimers has been calculated for a large number of linear and isosceles triangular configurations. In the latter configurations, the bond length of the reactant dimer has been kept fixed at its equilibrium value. Some typical potential energy surfaces of the linear trimers are shown in Figs. 1 to 3. As can be seen from these figures, all these surfaces exhibit a shallow potential well at small internuclear distances which extends into the entrance and exit valleys without an energy barrier. Moreover, for a given trimer $M'M_2$, the potential well is deeper (Figs. 1 and 2) when the lighter alkali atom occupies the central position. Variations of binding energy with respect to M'M bond length of the trimers in their isosceles triangular configurations, are shown in Fig. 4. Calculated values of binding energy and equilibrium bond lengths of the trimers are given in the Table which includes also the

results of Whitehead and Grice[6] for Li + Na_2 and Na + Li_2 reactions. These results show that the mixed alkali trimers are stable not only with respect to separated atoms but also with respect to atom-dimer dissociation. Moreover, the most stable configuration in each case is a linear one with the lighter alkali atom occupying the central position. This configuration is also symmetric in all cases excepting NaLiLi. It is interesting to

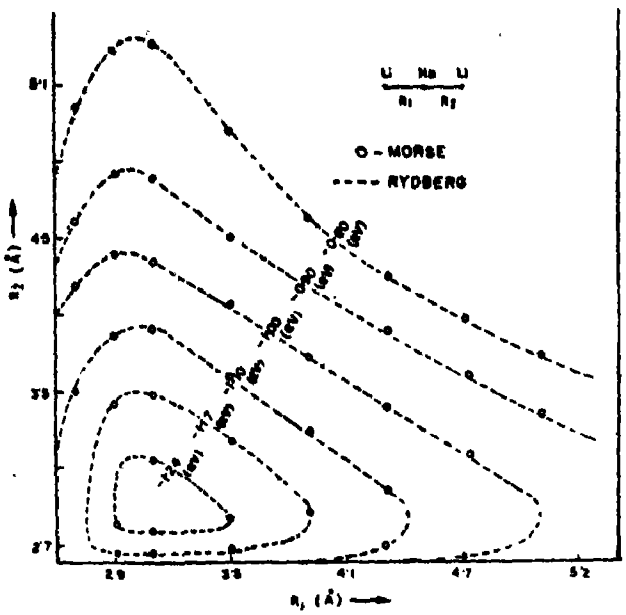


Fig. 1. Potential energy surfaces of LiNaLi for linear configuration.

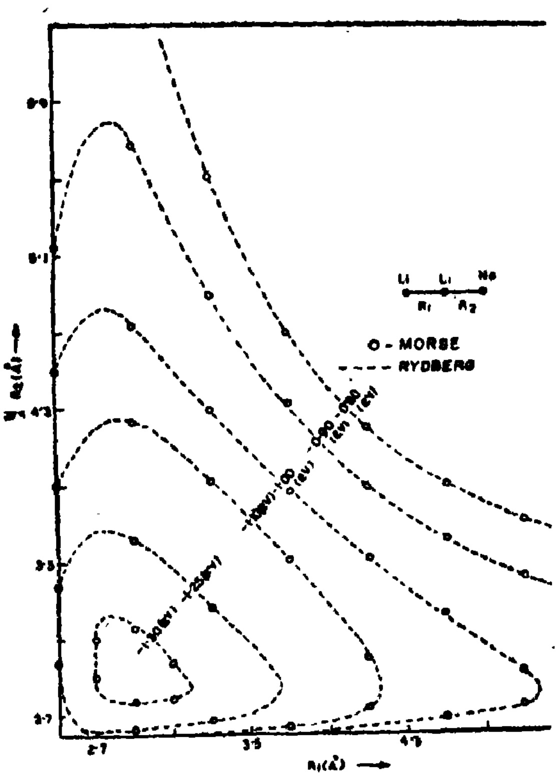


Fig. 2. Potential energy surfaces of LiLiNa for linear configuration.

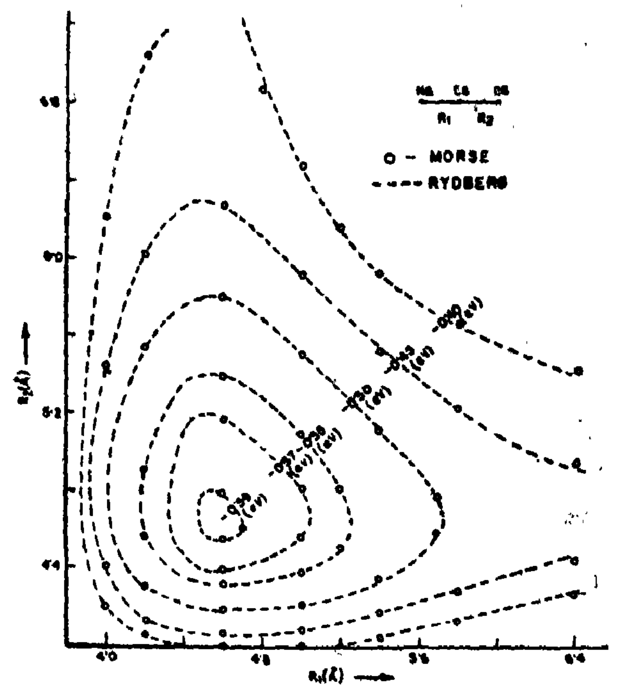


Fig. 3. Potential energy surfaces of NaCsCs for linear configuration.

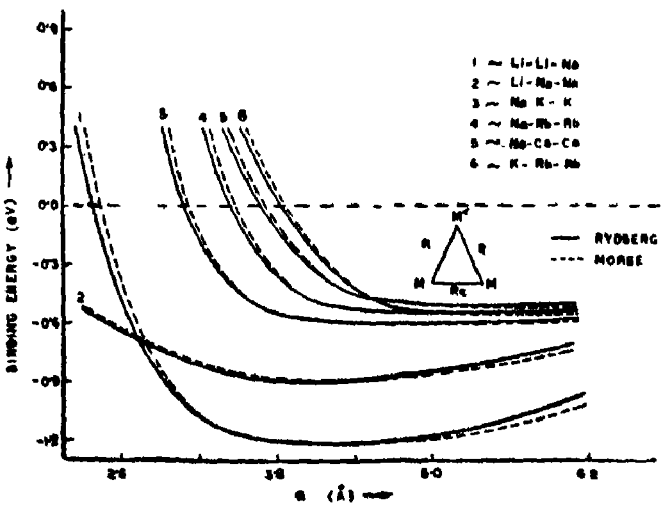


Fig. 4. Variation of binding energy with distance R of MMM′ system for isosceles triangular configuration.

note in this connection that the Morse and Rydberg potentials inspite of their different analytical forms yield almost identical result both for binding energy and geometry.

For lack of relevant experimental data or accurate ab initio calculations on these systems it is not possible to test the quantitative accuracy of the present calculations. A comparison with the results of Whitehead and Grice[6] which are obtained by the use of more accurate diatomic potentials, may be therefore of some interest. While comparing these results (see Table) with the present ones, we find that there is a very good agreement in bond lengths, but the binding energy values in some cases are over-estimated by about 2 Kcal/mole.

TABLE 1 : CALCULATED VALUES OF BINDING ENERGY (Δ) AND BOND LENGTHS (R_{AB}, R_{BC}) OF SOME MIXED ALKALI TRIMERS IN LINEAR AND ISOSCELES TRIANGULAR CONFIGURATIONS. [a]

A + BC → ABC → AB + C	− Δ(Kcal/mole)		R_{AB} (Å)		R_{BC} (Å)	
	Morse	Rydberg	Morse	Rydberg	Morse	Rydberg
$Na + Li_2 \rightarrow NaLiLi$	10.80(89)	10.84	3.10(3.18)	3.10	2.90(2.79)	2.90
$\rightarrow NaLi + Li$	7.70(7.4)	7.72	3.80(3.74)	3.80	2.67(2.67)	2.67
$Na + Li_2 \rightarrow LiNaLi$	8.71(6.8)	8.76	3.05(3.11)	3.05	3.05(3.11)	3.05
$\rightarrow LiNa + Li$	— —	—	— —	—	— —	—
$Li + Na_2 \rightarrow LiNaNa$	5.99(4.2)	6.00	3.03(3.08)	3.00	3.22(3.39)	3.25
$\rightarrow LiNa + Na$	0.72(0.9)	0.72	3.80(3.74)	3.80	3.08(3.08)	3.08
$Li + Na_2 \rightarrow NaLiNa$	7.64(5.7)	7.68	3.07(3.10)	3.10	3.07(3.10)	3.10
$\rightarrow NaLi + Na$	— —	—	— —	—	— —	—
$Na + K_2 \rightarrow NaKK$	4.35	4.38	3.80	3.80	4.10	4.10
$\rightarrow NaK + K$	2.75	2.77	3.83	4.83	3.92	3.92
$Na + K_2 \rightarrow KNaK$	6.19	6.23	3.91	3.93	3.91	3.93
$\rightarrow KNa + K$	— —	—	— —	-	—	—
$Na + Rb_2 \rightarrow NaRbRb$	4.15	4.15	4.10	4.10	4.40	4.42
$\rightarrow NaRb + Rb$	2.63	2.63	5.05	5.05	4.33	4.33
$Na + Rb_2 \rightarrow RbNaRb$	5.75	5.77	4.15	4.15	4.15	4.15
$\rightarrow RbNa + Rb$	—	—	—	—	—	—
$Na + Cs_2 \rightarrow NaCsCs$	3.90	3.92	4.35	4.40	4.80	4.75
$\rightarrow NaCs + Cs$	2.50	2.50	6.90	6.88	4.66	4.66
$Na + Cs_2 \rightarrow CsNaCs$	4.36	4.38	4.50	4.52	4.50	4.52
$\rightarrow CsNa + Cs$	—	—	—	—	—	—
$K + Rb_2 \rightarrow KRbRb$	4.25	4.27	4.30	4.30	4.50	4.50
$\rightarrow KRb + Rb$	3.45	3.46	5.35	5.35	4.33	4.33
$K + Rb_2 \rightarrow RbKRb$	4.61	4.65	4.40	4.40	4.40	4.40
$\rightarrow RbK + Rb$	—	—	—	—	—	—

a The upper and lower value for each M′MM system corresponds to linear and isosceles triangular configurations respectively. Values in the parentheses refer to those of Whitehead and Grice. These authors used a value of 23.75 Kcal/mole for the binding energy of Li_2, whereas the value used by us is 24.21 Kcal/mole. The difference is the zero-point energy of Li_2. The binding energy values are with respect to atom-dimer dissociation.

These authors have, however, remarked that their calculations might underestimate the stability of alkali trimers. In view of the fact that both of these calculations are based on London's equation which involves many approximations, a rigorous quantitative comparison is not of much significance. It is, however, expected that the qualitative features of all possible alkali atom–dimer exchange reactions can be understood from the present type of calculations.

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Photoperoxidation of Anthracene Sulphonates

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Oxygen quenching of excited singlet state of anthracene sulphonate (1-mono sulphonate (1AS), 2- mono sulphonate (2AS) and 1,5- di sulphonate (1,5AS)) and their photoperoxidation are studied in aqeous medium. Oxygen quenching constant is found to be nearly the same within the experimental error for different anthracene sulphonates. Theoretically calculated rate constant for oxygen quenching of fluorescence is compared with those obtained experimentally. However photoperoxidation is highly sensitive to number and position of the sulphonate group in the ring. The rate constant for peroxidation step is found to follow the order 1AS > 2 AS > 1,5AS and involve singlet oxygen.

IN presence of oxygen, anthracene photooxidises most readily in solvents such as carbon disulphide, chloroform or bromobenzene where its fluorescence quantum yield is very low[1]. In all these photooxidation reactions anthracene forms 1:1 transannular peroxides[2]. It has been well established that the singlet excited oxygen ($^1\Delta_g O_2$) is the reactive species, a mechanism which was initially proposed by Kautsky in 1930[3-5]. With acceptors like aromatic hydrocarbons or cis-dienes, singlet oxygen behaves like a good dienophile and the reaction is similar to Diels-Alder addition. Anthracene is known to react with singlet oxygen as well as with other dienophiles wheras naphthalene is unreactive toward singlet oxygen and toward most potent dienophiles[6,7]. the most direct evidence for participation of singlet oxygen has been provided by Corey and Taylor who generated $^1\Delta_g O_2$ by rf discharge in presence of anthracene and obtained anthracene peroxide as reaction product.

Nucleophilic as well as electrophilic substitution on anthracene ring is likely to change the oxidation potential of anthracene. This change is expected to be reflected in the efficiency of $^1\Delta_g O_2$ reaction with substituted anthracene[8]. It was considered of interest to study the effect of substitution of sulphonate groups at various positions of the anthracene ring on direct photooxidation reaction with a view to get a better understanding of its mechanism. The substitution makes the compounds water soluble and has profound effect on fluorescence[9] and infrared spectra[10] of the compounds although absorption spectra are only slightly perturbed.

Experimental

Anthracene 1-, 2-mono and 1,5-disulphonates were prepared by reducing corresponding anthraquinones with Zn-dust and 20% NH_4OH for 4-6 hrs. The products were treated with active animal charcoal to remove traces of anthraquinones and other impurities. Anthracene sulphonates were crystallized three to four times from water and obtained as sodium salt. The ease of reduction of different anthraquinone sulphonates were in the order : anthraquinone-1, 5-disulphonate > anthraquinone-2-mono sulphonate > anthraquinone-1-mono sulphonate.

Photochemical reactions were carried out in a specially designed cell immersed in a thermostat and kept in a dark room. Solutions were stirred during exposure and oxygen or air, as required by the experiment, was bubbled through it. Temperature was maintained at 30° ± 0.5. The stabilized light source was a 300-watt Hanovia type 507/7 Hg discharge tube contained in a blackened box with a window towards the reaction vessel. A Wood's glass filter was used to isolate 365 nm radiation. The OD were measured with a Beckmann DU Spectrophotometer model 4700. Ferrioxalate actinometry was done to standardise the light source. The fluorescence measurements were made with the Brice-Phoenix Universal Light Scattering Photometer Model 1000 Series. A high pressure mercury discharge lamp type AH-3, 85 watts with 365 nm filter was used as the exciting source and observations were made at 45° to the direction of incidence. The fluorescence spectra were measured in Beckmann spectrophotometer model DU 4700 with spectrofluorometer attachment.

Results and Discussion

Oxygen Quenching of Fluorescene : The Stern-Volmer oxygen quenching constant K_Q is related to the rate constant for oxygen quenching k_8 by the expression $k_8 = K_Q/\tau$, where τ is the actual lifetime of the fluorescent molecule in absence of oxygen and can be calculated from the knowledge of quantum yield of fluorescence ϕ°_f in deoxygenated solution and mean natural radiative lifetime τ° by the relationship $\tau = \tau^\circ \phi^\circ_f$.

Since for anthracene-1-sulphonate and anthracene-2-sulphonate, the mirror image relationship does not hold, an expression due to Strickler and Berg[11] was used to

* nee' Rohatgi

measure τ°. The expression is :

$$1/\tau^{\circ}=2.88\times10^{-9}\frac{g_l}{g_u}\frac{n_f^{3}}{n_a}\frac{\int F d\bar{\nu}}{\int \frac{F d\bar{\nu}}{\bar{\nu}^{3}}}\int\frac{\epsilon d\bar{\nu}}{\bar{\nu}}$$

where n_f and n_a are the mean refractive indices of the solvent over the fluorescence and absorption bands, $F(\bar{\nu})$ is relative fluorescence quantum intensity at wave number $(\bar{\nu})$ cm^{-1}. For singlet-singlet transition $g_l = g_u = 1$. Here it is assumed that $n_f = n_a$. The values so calculated from the absorption and fluorescence spectra are given in Table 1. The quantum yield of fluorescence ϕ°_f were determined by using anthracence in benzene as the fluorescence standard under condition of equal optical densities. Assuming oxygen quenching of singlet excited state to be diffusion controlled process the quenching rate constant k_3 can also be calculated from the expression

$k_3 = \frac{8RT}{2000\eta}$(where η is the viscosity of solvent, R the gas constant and T the temperature in Kelvin)

The calculated value for aqueous solution at 30° works out to be $1.26\times10^{10} M^{-1}s^{-1}$. The discrepancy between calculated and experimental value (Table 1) of k_3 may be due to larger sphere of quenching action than the collisional separation and also due to approximation inherent in the above equation. The failure of above equation in predicting the quenching rate constant apparently lies in the fact that Stokes-Einstein equation underestimates the diffusion coefficient of small molecule like oxygen. A better expression for rate constant of diffusion process is given as

$$k_3 = 4\pi N'(D_A + D_B)\sigma_{AB}$$

where N' is the number of molecules in millimole, D_A and D_B diffusion coefficients of reacting molecules and σ_{AB} the encounter distance. Estimation of molecular radius (r_A) of anthracene sulphonate from its molar volume, (calculated from its density) and substitution of r_A into the Stokes-Einstein equation, $D_A = kT/6\pi r_A \eta$, yields the diffusion coefficient of anthracene sulphonate in water.

	r_A in Å	D_A in cm^2s^{-1}
Anthracene 1 sulphonate	4.27	0.64×10^{-5}
Anthracene 2 sulphonate	4.27	0.64×10^{-5}
Anthracene 1,5-sulphonate	4.63	0.59×10^{-5}

Knowing the molcular radius of oxygen $r_{O_2} = 2$Å, its diffusion coefficient $D_{O_2} = 5\times10^{-5}$ cm^2s^{-1} [12], and assuming that $\sigma_{AB} = r_A + r_B$, k_3 is calculated and is given in Table 1 column 8.

Oxygen quenches the fluorescene of a large number of organic molecules. In most of the cases the quenching reaction step is diffusion controlled. Various types of interaction between O_2 and excited organic molecule are theoretically possible.

$$^1A^* + {}^3O_2 \rightarrow {}^3A + {}^1O_2 \quad \text{(I)}$$

$$^1A^* + {}^3O_2 \rightarrow {}^3A + {}^3O_2 \quad \text{(II)}$$

$$^1A^* + {}^3O_2 \rightarrow {}^1A + {}^3O_2 \quad \text{(III)}$$

TABLE 1

Compounds	τ^0_{ns}	ϕ^0_f	$k_1\times10^{-7}$ s^{-1}	$k_2\times10^{-8}$ s^{-1}	K_Q lM^{-1}	$k_3\times10^{-10}$ $lM^{-1}s^{-1}$	$k_3\times10^{-10}$ $lM^{-1}s^{-1}$ (Calculated)
1 ASO_3^-	13.7	0.25	7.3	2.2	150	4.2	2.6
2 ASO_3^-	11.8	0.40	8.4	1.3	200	4.2	2.6
1,5 $A(SO_3^-)_2$	14.5	0.26	6.9	2.0	190	5.0	2.8

From the observation of Parmenter and Rau[13] that aromatic hydrocarbons are quenched by O_2 at the same rate regardless of singlet-triplet energy gap, it appears that mechanism (I) is probably not involved. Stevens[14] has shown from kinetic studies that the mechanism (II) is the most important one for oxygen quenching of singlet excited state. Pulsed laser studies of Potashnick et al[15] and of Tibilov et al[16] also confirm the above view. Recently Stevens and Ors[17] have shown that 9, 10 dimethylanthracene and rubrene which have high fluorescence yield, steps (I) and (II) are equally probable. However this is not the case with anthracene sulphonates which have low fluorescence yield and step (II) is the important one. For aromatic hydrocarbon the step (III) does not generally occur as ϕ_f and ϕ_{ISC} normally add up to unity, where ϕ_{ISC} is the quantum yield for intersystem crossing ($= \phi_T$)[18-20].

Photoperoxidation : Anthracene sulphonates are water soluble compounds. They undergo photodimerization in aqueous solution in absence of oxygen, just like the parent compound in benzene. When exposed

to sunlight in presence of dissolved oxgen quantitative conversion to endoperoxide is observed (Fig. 1). The absorption spectrum of photoproduct is similar to that obtained by Gillet[21] for anthracene peroxide. The liberation of iodine on treating the irradiated solution with KI gives further support for peroxide mechanism[22]. The complete quenching of photoreaction on addition of NaN_3 indicates the involvement of $O_2\,^1\Delta_g$ since NaN_3 is a good quencher for $O_2\,^1\Delta_g$[23]. Works of Stevens[14] on photoperoxidation and of Kawaoka et al[24] on theoretical study of oxygen quenching of organic triplet state reveals that oxygen quenching of triplet state leads to singlet oxygen formation

$$^3A + {}^3O_2 \rightarrow {}^1O_2(^1\Delta_g) + A$$

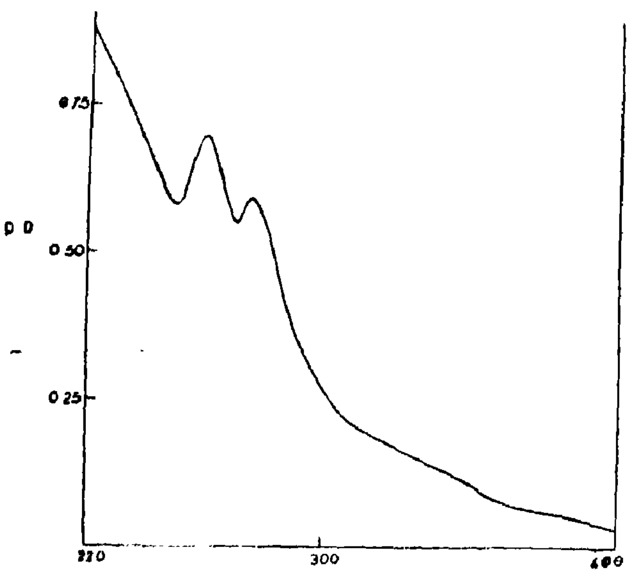


Fig. 1.: Absorption spectra for photoproduct obtained by exposing the 1 ASO_3^- solution to sun ray.

The various steps that can be visualized for the photophysical and photochemical processes occurring in the aerated solution of anthracene sulphonates can be represented as follows

$$A + h\nu \xrightarrow{I_0} A^*$$

$$A^* \xrightarrow{k_1} A + h\nu_f$$

$$A^* \xrightarrow{k_2} {}^3A$$

$$A^* + {}^3O_2 \xrightarrow{k_3} {}^3A + {}^3O_2$$

$$^3A \xrightarrow{k_4} A$$

$$^3A + {}^3O_2 \xrightarrow{k_5} A + {}^1O_2$$

$$A + {}^1O_2 \xrightarrow{k_6} AO_2$$

$$^1O_2^* \xrightarrow{k_7} {}^3O_2$$

From these steps, the quantum yield for photoperoxidation based on substrate disappearance assuming that photodimer formation is negligible under these conditions (the absence of photodimer in presence of oxygen is explained by the fact that O_2 quenches the excimer so that no dimer can be formed in its presence[16]) is given by the expression :

$$\phi_{AO_2} = \frac{k_6[A]}{k_6[A] + k_7} \times \frac{k_5[O_2]}{k_5[O_2] + k_4} \times \frac{k_2 + k_3[O_2]}{k_1 + k_2 + k_3[O_2]} \quad (1)$$

From spin statistical consideration, oxygen quenching rate constant for the triplet state k_5 should be 1/9 of the diffusion controlled rate[14] and therefore $k_5 \simeq 10^9$ $M^{-1}s^{-1}$. In oxygen saturated solution at atmospheric pressure $[O_2] = 3 \times 10^{-3}M$. Taking k_4 to be of the order of 10^3 s^{-1}[25], we have $k_5[O_2] >> k_4$. Hence $k_5[O_2]/(k_4 + k_5[O_2]) \simeq 1$. The factor $(k_2 + k_3[O_2])/(k_1 + k_2 + k_3[O_2])$ is triplet yield ϕ_T in presence of O_2. Eqn. (1) can be rearranged as

$$1/\phi_{AO_2} = 1/\phi_T + \frac{k_7}{k_6\phi_T} \times \frac{1}{[A]}$$

The plot of $1/\phi_{AO_2}$ vs. $1/[A]$ for 1-ASO_3^- and 2-ASO_3^- gives k_7/k_6 and ϕ_T (Fig. 2, Table 2). ϕ_T calculated from k_1, k_2 and k_3 obtained separately from

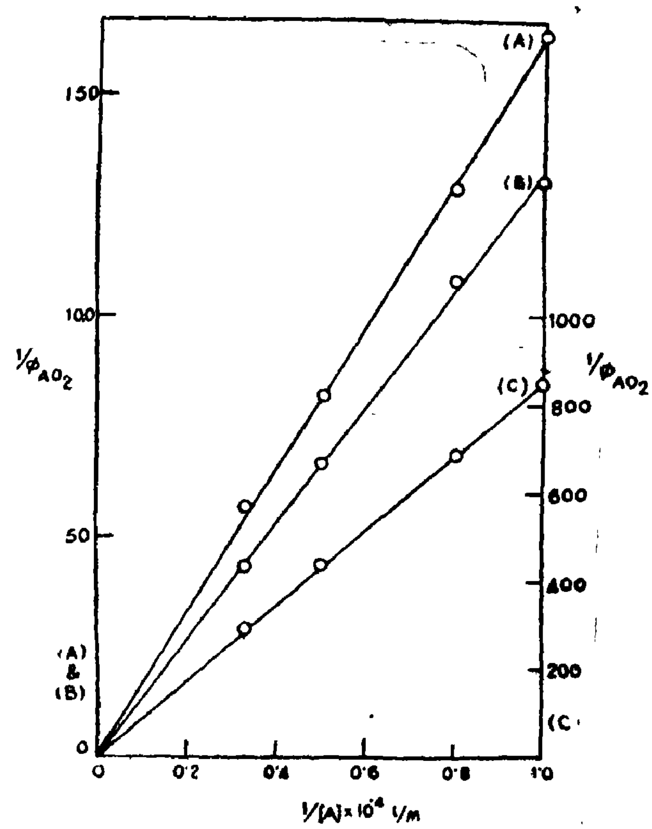


Fig. 2.: Plot for $1/\phi_{AO_2}$ vs. $1/[A]$

(A) 2 ASO_3^-
(B) 1 ASO_3^-
(C) 1,5 $A(SO_3^-)_2$

TABLE 2

Compound	k_7/k_8 mole l^{-1}	$k_8 \times 10^{-7}$ l. mole^{-1}s^{-1}	ϕ_T (exp) $[O_2] = 3\times10^{-4}$ M	ϕ_T (cal)		ϕ_{AO_2} ; $[A] = 10^{-4}$ M	
				$[O_2]$ 3×10^{-4} M	$[O_2]$ 6×10^{-4} M	$[O_2]$ 3×10^{-4} M	$[O_2]$ 6×10^{-4} M
1 ASO_3^-	0.92×10^{-3}	5.4	0.70	0.82	0.77	7.6×10^{-6}	9.0×10^{-6}
2 ASO_3^-	1.1×10^{-3}	4.5	0.70	0.81	0.73	6.2×10^{-6}	5.9×10^{-6}
1,5 $A(SO_3^-)_2$	7×10^{-3}	0.7	—	0.85	0.76	1.2×10^{-5}	1.0×10^{-5}

fluorescence measurement is in good agreement with the value obtained here. In case of 1, 5 $A(SO_3^-)_2$ inaccuracy in the measurement of ϕ_T from the intercept was avoided by using the calculated value of ϕ_T to get k_7/k_8 for this compound. There is very little $[O_2]$ dependence of ϕ_{AO_2}, presumably due to small dependence of ϕ_T on $[O_2]$ (Table 2). The oxidation of anthracene sulphonates are highly dependent on the number and position of the sulphonate groups. Sulphonate group is known to be an electron withdrawing group. So it shifts the oxidation potential of anthracene ring towards more negative value. k_8 agrees well with the reverse order of the ease of reduction of corresponding anthraquinone (see experimental) when k_7 is taken as 5×10^5 s^{-1} [26].

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Heterocyclic System III[1]. Conversion of Semicarbazones, N-Benzoylhydrazones and p-Nitrophenylhydrazones of 4-Oxo-4H-[1] Benzopyran-3-Carboxaldehydes to the Pyrazole System.

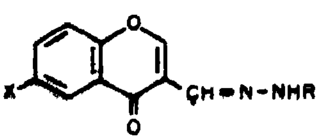
C. K. GHOSH* and K. K. MUKHOPADHYAY

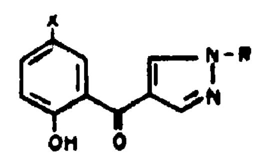
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The semicarbazones (III), N-benzoylhydrazones (IV) and p-nitrophenylhydrazones (V) of 4-Oxo-4H-[1] benzopyran-3-carboxaldehydes undergo rearrangement on being refluxed in ethylene glycol, the former two yielding 4-(2-hydroxybenzoyl)pyrazoles (VI) identical with the reaction products of hydrazine and the aforementioned carboxaldehydes, and the latter giving rise to 1-(p-nitrophenyl)-4-(2-hydroxybenzoyl)pyrazoles (VIII).

HYDRAZINE reacts with 4-Oxo-4H[1] benzopyran-3-carboxaldehydes (henceforth called as 3-formylchromones) to give directly 4-(2-hydroxybenzoyl)-pyrazoles (VI)[2], the intermediate hydrazones (I) not being isolable. Phenylhydrazones (II) of 3-formylchromones on being refluxed in either ethanolic potassium hydroxide[3] or acetic acid[1] furnish 1-phenyl-4-(2-hydroxybenzoyl)pyrazoles (VII). When refluxed in acetic acid, the hydrazones (II) undergo intramolecular nucleophilic attack at C-2 of the chromone moiety with concomitant opening of the pyrone ring so that the pyrazoles (VII) result in[1]. It was our interest to see whether this type of intramolecular nucleophilic attack is possible for the hydrazones (III-V) having hydrazino group of much weaker nucleophilicity. Successful conversion of the hydrazones (III-V) to the pyrazole system is reported herein.





I,	R=H	VI,	R=H
II,	R=Ph	VII,	R=Ph
III,	R=CONH$_2$	VIII,	R=C$_6$H$_4$-NO$_2$(p)
IV,	R=COC$_6$H$_5$		
V,	R=C$_6$H$_4$-NO$_2$(p)		

By refluxing a solution in glacial acetic acid, no change could be brought about in any of the hydrazones (III-V). In the rearrangements of the phenylhydrazones of α-β unsaturated carbonyl compounds to pyrazolines, to which the cyclisation reaction envisaged by us has formal analogy, it is uncertain to what extent the solubilities of the hydrazones influence the reaction[4]. It is anticipated that thermal energy rather than solubility mostly influences the aforementioned rearrangement. Our anticipation was proved to be correct when by refluxing in ethylene glycol (b. p. 200°) all the hydrazones (III-V) were converted to the pyrazole system.

The semicarbazones (III) when refluxed in ethylene glycol underwent rearrangement accompanied by hydrolytic removal of 1-carboxamido group to afford in 40-70% yield the same 4-(2-hydroxybenzoyl)pyrazoles (VI) as were obtained by reacting the proper 3-formylchromones with hydrazine. It may be noted that hydrolytic removal of 1-carboxamido group is often observed in the cyclisation reaction of the semicarbazones of α-β unsaturated aldehydes or ketones to pyrazolines[5]. The N-benzoylhydrazones (IV) on similar treatment also rearranged to the pyrazoles (VI) (yield 40-60%), the benzoyl group being knocked off. It would not be irrelevant to mention here that ethylene glycol-p-toluenesulfonic acid mixture can cause even aromatic deacetylation[6]. The p-nitrophenylhydrazones (V) on being refluxed in ethylene glycol produced 4-(2-hydroxybenzoyl)-pyrazoles (VIII) in 50-80% yield, the latter on oxidation with chromic acid giving 1-(p-nitrophenyl) pyrazole-4-carboxylic acid[7]. The different hydrazones (III-V) that were converted to the pyrazoles (VI and VIII) are shown in Table 1.

Experimental

All melting points are uncorrected. Elemental (C, H and N) analyses done for all the pyrazoles (VI and VIII), were in good agreement with the calculated values.

General method for the preparation of the hydrazones(III-V)

The semicarbazones(III) were prepared by adding a warm solution of semicarbazide hydrochloride (0.55 g, 0.005 mole) and sodium acetate (1.0 g) in water (2-3 ml) to a hot solution of the properly substituted 3-formylchromones[3,8] (0.005 mole) in ethanol(3-5 ml). N-Benzoylhydrazones(IV) and p-nitrophenylhydrazones(V) were prepared by refluxing 3-formylchromones in ethanol with equimolar amounts of benzoic hydrazide and p-nitrophenylhydrazine respectively.

TABLE 1—MELTING POINTS OF DIFFERENT HYDRAZONES (III-V)[a] AND THEIR REARRANGED PRODUCTS (VI AND VIII)[b]

Substituent X	Hydrazones (III)	(IV)	Pyrazoles (VI) obtd. from (III) and (IV)	Acetates[c] of (VI)	Hydrazones (V)	Pyrazoles (VIII) obtd. from (V)	Acetates[d] of pyrazoles (VIII)
H	240	207-8	124	115	248-50	188	150
CH_3	257-8	—	170	—	260	185	157
Cl	250	209	180	97	255	187	151
Br	230	222	170	112	252	190	158
NO_2	228	225	213	242-3	262	238	171

[a]The hydrazones (III-V) whenever recrystallised, were recrystallised from acetic acid.

[b]Recrystallised from ethanol or aqueous ethanol.

[c]All these acetates were recrystallised from benzene-pet. ether, and were characterised from their NMR spectra, the three protons of O—Ac coming as singlet at, say δ2.25 and those of N—Ac appearing at δ2.70 (singlet).

[d]Recrystallised from chloroform-pet. ether.

4-(2-Hydroxybenzoyl)pyrazole (VI, X=H) from chromone-3-carboxaldehydesemicarbazone (III, X=H).

The semicarbazone (III, X=H) (0.70 g) was refluxed in ethylene glycol (10 ml) for 6 hr, cooled and diluted with water. The precipitated solid was filtered and crystallised from acetone-water (charcoal) to afford the *pyrazole* (VI, X=H) (0.54 g), m.p. and m.m.p 124°, υ_{max} ($CHCl_3$) ; 3220 (w, br, NH), 3140 (w, br, OH chelated with carbonyl), 1622 (s, aryl pyrazolyl ketone chelated with OH). When refluxed with acetic anhydride and fused sodium acetate it gave a mixture of a monoacetate and a diacetate that were separated by fractional crystallisation from chloroform, the monoacetate precipitating out first as colorless crystals, m.p. 164°, τ($CDCl_3$) 1.63 (s, 1H, pyrazole H_3), 2.00 (s, 1H, pyrazole H_5), 2.43-2.99 (m, 5H, ArH and NH) and 7.83 (s, 3H, -O-$COCH_3$). The diacetate had m.p. 115° benzene-pet. ether) and showed NMR signals at τ($CDCl_3$) 1.55 (s, 1H, pyrazole H_3), 200 (s, 1H, pyrazole H_5), 2.27-2.97 (m, 4H, ArH), 7.28 (s, 3H, -N-$COCH_3$) and 7.80 (s, 3H, -O.$COCH_3$). For all other pyrazoles (VI) only the diacetates were obtained (Table 1).

Authentic sample of 4-(2-hydroxybenzoyl) pyrazole (VI, X=H)

To a hot ethanolic solution of 3-formylchromone (0.878 g, 0.005 mole) was added an aqueous solution of hydrazine prepared from hydrazine hydrochloride (0.52g, 0.005 mole) and sodium acetate (1.0 g), and the mixture warmed for 15 min, then it was cooled and diluted with water when the *pyrazole* (VI, X=H) (0.85 g), m.p. 122° was obtained.

All other semicarbazones (III) (Table 1) were similarly converted to the respective pyrazoles (VI), the identity of the latter being also confirmed by their independent synthesis from proper 3-formylchromones and hydrazine as described above.

Rearrangement of N-benzoylhydrazone (IV, X=H)

By refluxing a mixture of 3-formylchromone (0.35 g, 0.002 mole) and benzoic hydrazide (0.27 g, 0.002 mole), m.p. 75-80° was obtained the hydrazone (IV, X=H) (0.56 g), m.p. 207-208°, υ_{max} (KBr): 3425 (s, br, NH), 1645 (s, CONH- and -CH=N-) and 1625 cm^{-1} (pyrone carbonyl and -C=C-) (Found : C, 69.43 ; H, 4.32 ; N, 9.54 ; Calc. for $C_{17}H_{12}N_2O_3$: C, 69.52 ; H, 4.10 ; N, 9.59%). This hydrazone (0.56 g) on being refluxed in ethylene glycol afforded *4-(2-hydroxybenzoyl)pyrazole* (0.29 g), m.p. and m.m.p. 124°. All other hydrazones (IV) were similarly rearranged to the pyrazoles (VI).

1-(p-Nitrophenyl)-4-(2-hydroxy-5-bromobenzoyl)pyrazole (VIII, X=Br).

The experimental procedure for the cyclisation of the nitrophenylhydrazone (V, X=Br) to the pyrazole (VIII, X=Br) is described here as a representative case. A solution of the nitrophenylhydrazone (V, X=Br) (0.30 g) in ethylene glycol (10 ml) was refluxed for 8 hr, then cooled and diluted with water when the *pyrazole* (VIII, X=Br) (0.22 g), m.p. 190° (ethanol) was obtained. It showed IR absorption at 3115 (m, OH chelated with carbonyl), 1620 (s, diarylketone chelated with OH), and 1590 cm^{-1} (s, -C=N- and aromatic) in addition to two strong absorption bands at 1542 and 1332 cm^{-1} due to aromatic nitro group. Its *acetate* showed absorption peaks at 1757 (ester carbonyl), 1650 (keto-carbonyl), 1590 (-C=N- and aromatic), 1545 and 1332 (aromatic NO_2).

Oxidation of the pyrazoles (VIII)

Each of the pyrazoles (VIII) was oxidised with chromic acid in acetic acid-water-acetone mixture[1] to afford 1-(p-nitrophenyl)pyrazole-4-carboxylic acid, m.p. 245-8° ($CHCl_3$) (lit[7]., m.p. 250°).

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Synthetic and Spectroscopic Studies on 5-Carboxymethylthio-2-Arylamino-1,3,4-Thiadiazoles

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Twenty-seven new 5-carboxymethylthio-2-arylamino-1-,3,4-thiadiazoles have been synthesised by refluxing 5-mercapto-2-arylamino-1,3,4-thiadiazole sodium salts with monochloroacetic acid in dimethyl formamide.

THE fact that many thiadiazole derivatives like 5-(2-pyridyl)-1,3,4-thiadiazoline-2-thione[1] is an antitubercular agent; 2-amino-5-(alkyl-3-oxocyclopentyl)-1,3,4-thiadiazole thiosemicarbazone[2], 2-acetylamino-5-sulphamido-1,3,4-thiadiazole[3], 2-amino-1,3,4-thiadiazole[4], 2-ethylamino-1,3,4-thiadiazole[5] and 2-alkylamino-1,3,4-thiadiazole[6] have shown moderate tumour inhibitory properties; 2-amino-$\triangle^2$-1,3,4-thiadiazolin-5-one[7] and thiadiazolyl urea[8] have been reported to be herbicidal and 2-amino-1,3,4-thiadiazole[9] exhibit remarkable insecticidal properties led the authors to extend this work. We now report the synthesis of 5-carboxymethylthio-2-arylamino-1,3,4-thiadiazoles from several corresponding 5-mercapto-2-arylamino-1,3,4-thiadiazoles, with a view to studying their biological activity.

Results and Discussion

4-Arylthiosemicarbazides required as starting materials were synthesised by the method of Kazakov *et al.*[10], which on being refluxed with carbon disulphide in absolute ethanol gave 2-arylamino-5-mercapto-1,3,4-thiadiazoles[11-12].

The 5-carboxymethylthio-2-arylamino-1,3,4-thiadiazoles have been prepared by refluxing 5-mercapto-2-arylamino-1,3,4-thiadiazole sodium salts with monochloroacetic acid in dimethylformamide[13].

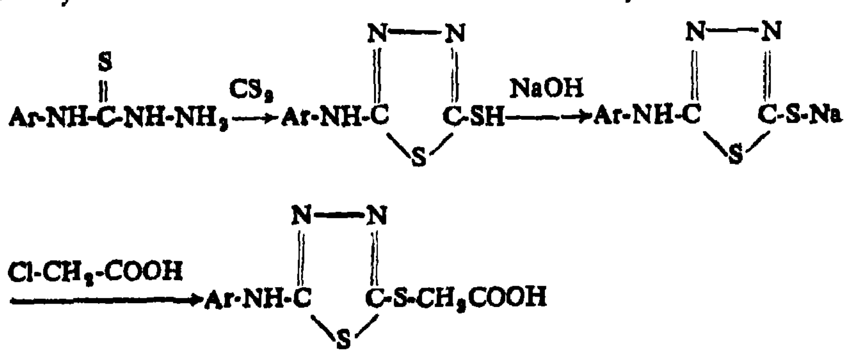
Spectroscopic Studies

U. V.: The ultraviolet spectra of several 5-carboxymethylthio-2-arylamino-1,3,4-thiadiazoles have been determined using ethanol and methanol as solvents. Absorption maxima of all these compounds have shown the characteristic peaks in the region between 210-420 mμ. It can be seen from the study of the U.V. absorption data that there is a marked bathochromic shift in the absorption bands due to introduction of carboxymethylthio group.

IR: Infrared spectra of several 5-carboxymethylthio-2-arylamino-1,3,4-thiadiazoles have been recorded. Characteristic absorption peaks show the presence of substituted phenyl, -NH_2, -COOH, cyclic C=N, cyclic N=C=S and cyclic C−S groups. The details of infrared absorptions of some compounds are enlisted in Table 1.

Experimental

U. V. spectra were measured in ethanol and methanol solvents. Spectra were recorded on Perkin-Elmer 202 Automatic Recording Spectrophotometer. IR spectra were recorded on Perkin-Elmer 720 infrared spectrophotometer and Perkin-Elmer 621 Grading infrared spectrophotometer. Solution spectra were measured in Nujol mulls and KBr disc. The compounds were analysed for carbon, hydrogen and nitrogen on



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TABLE 1. INFRARED ABSORPTIONS OF SOME 5-CARBOXYMETHYLTHIO-2-ARYLAMINO-1,3,4-THIADIAZOLES

	Compound	νNH	νCH_2	Cyclic νN=C=S	Cyclic νC=N	Cyclic νN–N=C	νS	νCOOH	Others
1.	5-Carboxymethyl-thio-2-*p*-fluoro-phenylamino 1,3,4-thiadiazole	3400	2930 1720	1450	1575	1265	1370 760	3220 1720	C-F 1200
2.	5-Carboxymethyl-thio-2-*o*-hydroxy-phenylamino-1,3,4-thiadiazole	3240	2930 2853	1470	1570	1265	1380 750	3200 2925 1625 1380	OH 3240 1380 1180
3.	5-Carboxymethyl-thio-2-*o*-anisylamino-1,3,4-thiadiazole	3225	2925 2853	1470	1565 1495	1260	1380 750	3200 1625 1380 1260	CH_3- 1440
4.	5-Carboxymethyl-thio-2-(2,4-dichlorophenyl)-amino-1,3,4-thiadiazole	3225	2850	1475	1596 1550	1255	1380 750	3225 1710 1675 1380	C-Cl 820
5.	5-Carboxymethyl-thio-2-(2-nitro-4-chlorophenyl) amino-1,3,4-thiadiazole	3400	2870	1475	1570	1260	1350 750	3230 1265	C-Cl 825 NO_2- 1575 1340

Coleman analyser and data were found well in agreement, within the limits of the possible experimental error, with calculated values. All the melting points were taken by the capillary method and are uncorrected. The purity of the compounds was tested by thin-layer chromatography.

5-Carboxymethylthio-2-arylamino-1,3,4-thiadiazoles

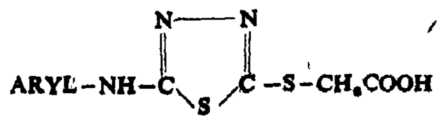
2-Arylamino-5-mercapto-1, 3, 4-thiadiazoles (0.01 mole) dissolved in sodium hydroxide (0.85g NaOH in 5 ml. water) and dimethyl formamide (10 ml.), was treated with monochloroacetic acid (0.01 mole) in sodium carbonate solution (1.75g Na_2CO_3 in 10 ml. water) and the mixture was refluxed on a water-bath for two hours. It was diluted with water (50 ml.), cooled, filtered and acidified with concentrated hydrochloric acid. The resultant precipitate was collected by filtration, washed well with water, dried and recrystallised from glacial acetic acid to give shining needle-shaped crystals.

Twenty six new 5-carboxymethylthio-2-arylamino-1,3,4-thiadiazoles were synthesised using the above general method. The yields, m.p.s and analytical data of these compounds are described in Table 2.

2-Arylamino-5-mercapto-1,3,4-thiadiazoles

A mixture of 4-arylthiosemicarbazides (0.06 mole), carbon disulphide (0.06 mole) and absolute ethanol (25 ml.) was refluxed in a 250 ml. flask on a water-bath at 65-70° for two hours. Excess alcohol was distilled off under reduced pressure and residue after cooling was poured into ice-cold water. The solid which separated was filtered, washed well with water, dried and recrystallised from absolute ethanol.

TABLE 2. 2-ARYLAMINO-5-CARBOXYMETHYLTHIO-1,3,4-THIADIAZOLES



S. No.	*ARYL* GROUP	Molecular formula	Yield %	m. p. °C	ANALYSES	%C	%H	%N
1.	Phenyl	$C_{10}H_9N_3S_2O_2$	70	120	Found	44.80	3.24	15.86
					Calc.	44.94	3.37	15.73
2.	*o*-Tolyl	$C_{11}H_{11}N_3S_2O_2$	75	130	Found	47.18	3.86	14.72
					Calc.	46.97	3.91	14.95
3.	*p*-Tolyl	$C_{11}H_{11}N_3S_2O_2$	65	205	Found	46.82	3.74	14.81
					Calc.	46.97	3.91	14.95
4.	*p* Fluorophenyl	$C_{10}H_8N_3S_2FO_2$	72	130	Fonnd	41.86	2.64	14.85
					Calc.	42.10	2.81	14.74
5.	*p*-Chlorophenyl	$C_{10}H_8N_3S_2ClO_2$	58	105	Found	39.96	2.78	13.75
					Calc.	39.80	2.65	13.93
6.	*p*-Bromophenyl	$C_{10}H_8N_3S_2BrO_2$	72	140	Found	42.32	2.94	14.86
					Calc.	42.10	2.81	14.74
7.	*o*-Anisyl	$C_{11}H_{11}N_3S_2O_3$	63	165	Found	44.28	3.92	14.06
					Calc.	44.44	3.70	14.14
8.	*m*-Anisyl	$C_{11}H_{11}N_3S_2O_3$	60	185	Found	44.67	3.84	14.23
					Calc.	44.44	3.70	14.14
9.	*p*-Anisyl	$C_{11}H_{11}N_3S_2O_3$	68	85	Found	44 52	3.65	14.27
					Calc.	44.44	3.70	14.14
10.	*o*-Phenetyl	$C_{12}H_{13}N_3S_2O_3$	60	145	Found	43.94	3.82	12.91
					Calc.	43.77	3.95	12.76
11.	*m*-Phenetyl	$C_{12}H_{13}N_3S_2O_3$	70	130	Found	43.62	3.88	12.76
					Calc.	43.77	3.95	12.76
12.	*p*-Phenethyl	$C_{12}H_{13}N_3S_2O_3$	72	160	Found	43.73	3.95	12.62
					Calc.	43.77	3.95	12.76
13.	*o*-Hydroxyphenyl	$C_{10}H_9N_3S_2O_3$	70	150	Found	42.25	3.24	14.68
					Calc.	42.40	3.18	14.84
14.	*p*-Hydroxyphenyl	$C_{10}H_9N_3S_2O_3$	72	110	Found	42.54	3.06	14.84
					Calc.	42.40	3.18	14.84
15.	*o*-Nitrophenyl	$C_{10}H_8N_4S_2O_4$	60	62-65	Found	38.41	2.38	17.82
					Calc.	38.46	2.56	17.95
16.	2,4-Dichlorophenyl	$C_{10}H_7N_3S_2Cl_2O_2$	62	152	Found	35.52	2.24	12.65
					Calc.	35.71	2.08	12.50
17.	2,5-Dichlorophenyl	$C_{10}H_7N_3S_2Cl_2O_2$	55	42	Found	35.96	2.16	12.34
					Calc.	35.71	2.08	12.50
18.	2-Nitro-4-chlorophenyl	$C_{10}H_7N_4S_2ClO_4$	62	110	Found	34.68	2.29	16.33
					Calc.	34.63	2.02	16.16
19.	2-Chloro-4-nitrophenyl	$C_{10}H_7N_4S_2ClO_4$	60	115	Found	34.85	2.17	16.24
					Calc.	34.63	2.02	16.16
20.	*m*-Cresolyl	$C_{11}H_{11}N_3S_2O_4$	55	135	Found	44.28	3.58	14.32
					Calc.	44.44	3.70	14.14
21.	1-Naphthyl	$C_{14}H_{11}N_3S_2O_2$	70	160	Found	52 81	3.26	13.51
					Calc.	52.99	3.47	13.25
22.	2-Naphthyl	$C_{14}H_{11}N_3S_2O_2$	69	165	Found	52 86	3.56	13.42
					Calc.	52.99	3.47	13 25
23.	2-Thiazolyl	$C_7H_6N_4S_3O_2$	60	170-172	Found	32.48	2.46	16.32
					Calc.	32.31	2.31	16.15
24.	Benzothiazolyl	$C_{11}H_8N_4S_3O_2$	58	83-85	Found	49.61	2.32	17.45
					Calc.	40.74	2.47	17.28
25.	Benzyl	$C_{11}H_{11}N_3S_2O_2$	75	168-170	Found	46.86	3.77	14.76
					Calc.	46.97	3.91	14.95
26.	Cyclohexyl	$C_{10}H_{15}N_3S_2O_2$	72	110	Found	41.34	5.35	13.38
					Calc.	41.52	5.19	14.53

Acknowledgement

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Studies on Potential Pesticides. Part VIII Synthesis of O,O-Dialkyl S-[2-(Phenoxymethyl)-1,3,4-Oxadiazolyl-5-] Dithiophosphate and O,O-Dialkyl O-[2-(Phenoxymethyl)-1,3,4-Oxadiazol-5-Thione-4-Methyl-] Dithiophosphate.

ANIL K. SENGUPTA and O. P. BAJAJ

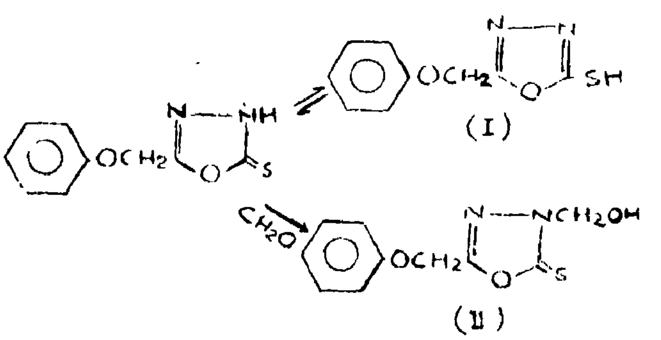
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Manuscript received 19 February 1977, accepted 17 May 1977.

Twenty three new organophosphourous compounds have been synthesised by the condensation of O,O-dialkyl chlorothio-phosphate with several 2-phenoxymethyl-5-mercapto 1,3,4-oxadiazole and 2-phenoxymethyl 4-hydroxymethyl 1,3,4-oxadiazole 5-thione. Nine compounds were tested for their anti-acetyl-cholinesterase activity.

ORGANOPHOSPHATES exhibiting potent anti-acetyl cholinesterase activities[1,2] have been used extensively as important insecticides[3,4]. The insecticidal properties of condensation products of chloromethyl-1,3,4-oxadiazole and thiadiazoles with potassium dialkyl phosphorothiolothionates were reported[5]. A number of oxadiazole compounds were reported as insecticides, miticides and bactericides[6,7]. Recently Sengupta *et al.* observed the bactericidal properties of oxadiazole derivatives. Pianka reported the pesticidal properties of organophosphorous compounds containing oxadiazole and thiazoles[8,9]. With a view to study the acetyl cholinesterase inhibition properties and insecticidal activity, we synthesised several compounds by condensing O, O-dialkyl chlorothio phosphate with several 2-phenoxy methyl-5-mercapto 1,3,4-oxadiazole and 2-phenoxy methyl 4-hydroxymethyl 1,3,4-oxadiazole-5-thione.

In all twenty three compounds have been synthesised by replacing the active hydrogen of I and II by O,O-dialkyl chlorothiophosphate.



(I)

(II)

The detailed activity of these compounds will be published elsewhere.

Experimental

0,0-dialkyl chlorothiophosphate was prepared according to the method of Fletcher *et al*[10]. Thiophosphorylchloride was prepared after the method of Belar[11].

0,0-Dipropyl chlorothiophosphate

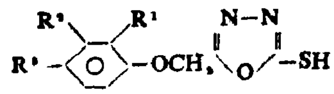
Thiophosphorylchloride (20 g) in dry benzene (50 ml) was added under constant stirring to a solution of sodium n-propoxide (from 5.5 g of Na in 75 ml of propanol). The reaction temperature being kept at 5-10°. After complete addition the mixture was filtered and filtrate concentrated in vacuum. The product distilled at 130/3 mm. yield 50%.

2(2,4 Dichloro phenoxymethyl) 1,3,4-oxadiazol-5-thiones was synthesised following Youngs method[12]. A suspension of 0.1 mole of 2,4-Dichloro phenoxyacetic acid hydrazide, 0.1 mole of potassium hydroxide and .11 mole of carbondisulphide was refluxed on steam-bath for twelve hours. The reaction mixture cooled, solvent distilled off and residue dissolved in water and acidified with dilute hydrochloric acid; solid obtained was crystallised from ethanol. Other thiones were synthesised by the similar method. The analysis, m.p.s are recorded in Table 1.

4-hydroxymethyl-2-(-4-chlorophenoxymethyl)-1,3,4-oxadiazol-5-thione.

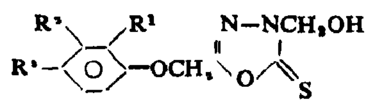
To a suspension of 0.1 mole of 2-(4-chlorophenoxymethyl)-1,3,4-oxadiazol-5-thione in 100 ml ethanol was added 1.0 g (40%) formaldehyde. The reaction mixture was left overnight at room temperature, separated solid was filtered and crystallised from ethanol. M.P. and analysis of the title compounds are recorded in Table 2.

TABLE 1



Compd. no.	R[1]	R[2]	R[3]	M.P.°C	Molecular formula	% of N Found	Calcd.
1.	Cl	H	Cl	147	$C_9H_6Cl_2N_2O_2S$	10.68	10.11
2.	H	H	Cl	159	$C_9H_7ClN_2O_2S$	12.01	11.57
3.	CH_3	H	H	121	$C_{10}H_{10}N_2O_2S$	12.26	12.61
4.	H	CH_3	H	96-7	$C_{10}H_{10}N_2O_2S$	12.84	12.61
5.	H	H	CH_3	149	$C_{10}H_{10}N_2O_2S$	12 78	12.61

TABLE 2



Compd. No.	R[1]	R[2]	R[3]	M.P.°C	Molecular formula	% of N Found	Calcd.
1.	Cl	H	Cl	137	$C_{10}H_8Cl_2N_2O_3S$	9.48	9.12
2.	H	H	Cl	123	$C_{10}H_9ClN_2O_3S$	10.15	10.29
3.	CH_3	H	H	100-1	$C_{11}H_{12}N_2O_3S$	11.42	11.11
4.	H	CH_3	H	79-81	$C_{11}H_{12}N_2O_3S$	11.24	11.11
5.	H	H	CH_3	124	$C_{11}H_{12}N_2O_3S$	11.34	11.11

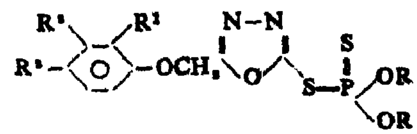
O,O-dialkyl S-[2-(p-methyl phenoxymethyl) 1, 3, 4-oxadiazolyl-5-] dithiophosphate

A mixture of corresponding O,O-dialkyl chlorothiophosphate (1 *M*) and 5-mercapto 2-(*p*-methyl phenoxymethyl) 1,3,4-oxadiazole (1 *M*) was refluxed in dry acetone for twelve hours under stirring in the presence of anhydrous potassium carbonate. Filtered and solvent was removed under reduced pressure. Solid obtained was crystallised from ethyl alcohol M.p.s are recorded in table 3.

O,O-dialkyl O-2(p-chloro phenoxymethyl-1,3,4-oxadiazol-5-thione-4-methyl) dithiophosphate.

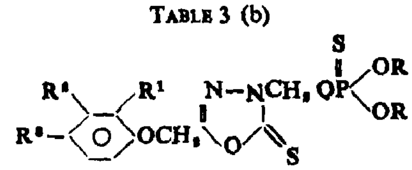
Mixture of corresponding O,O-dialkyl chlorothiophosphate (0.01 M) and 4-hydroxymethyl [2-(*p*-chloro phenoxymethyl)-1,3,4-oxadiazol]-5-thione in dry acetone was refluxed in presence of anhydrous potassium carbonate for twelve hours under stirring. Filtered and solvent was removed under reduced pressure. Solid obtained was crystallised from ethyl acetate, M.p.s are recorded in Table 3.

TABLE 3 (a)



Comp. No.	R^1	R^2	R^3	R	M.P.°C	Molecular formula
1.	Cl	H	Cl	C_2H_5	191-93	$C_{13}H_{15}Cl_2N_2O_4PS_2$
2.	H	H	Cl	C_2H_5	197-99	$C_{13}H_{16}ClN_2O_4PS_2$
3.	CH_3	H	H	C_2H_5	176	$C_{14}H_{19}N_2O_4PS_2$
4.	H	H	CH_3	C_2H_5	212-14	$C_{14}H_{19}N_2O_4PS_2$
5.	Cl	H	Cl	nC_3H_7	189	$C_{15}H_{19}Cl_2N_2O_4PS_2$
6.	H	H	Cl	nC_3H_7	212	$C_{15}H_{20}ClN_2O_4PS_2$
7.	CH_3	H	H	nC_3H_7	185-86	$C_{16}H_{23}N_2O_4PS_2$
8.	H	H	CH_3	nC_3H_7	204	$C_{16}H_{23}N_2O_4PS_2$
9.	Cl	H	Cl	nC_4H_9	184	$C_{17}H_{23}Cl_2N_2O_4PS_2$
10.	H	H	Cl	nC_4H_9	188-90	$C_{17}H_{24}ClN_2O_4PS_2$
11.	CH_3	H	H	nC_4H_9	201-3	$C_{18}H_{27}N_2O_4PS_2$
12.	H	H	CH_3	nC_4H_9	222-3	$C_{18}H_{27}N_2O_4PS_2$

TABLE 3 (b)



Comp. No.	R^1	R^2	R^3	R	M.P.°C	Molecular formula
13.	Cl	H	Cl	C_2H_5	189	$C_{14}H_{17}Cl_2N_2O_5PS_2$
14.	H	H	Cl	C_2H_5	200-2	$C_{14}H_{18}ClN_2O_5PS_2$
15.	CH_3	H	H	C_2H_5	178	$C_{15}H_{21}N_2O_5PS_2$
16.	H	H	CH_3	C_2H_5	182	$C_{15}H_{21}N_2O_5PS_2$
17.	Cl	H	Cl	nC_3H_7	211	$C_{16}H_{21}Cl_2N_2O_5PS_2$
18.	H	H	Cl	nC_3H_7	204	$C_{16}H_{22}ClN_2O_5PS_2$
19.	CH_3	H	H	nC_3H_7	167	$C_{17}H_{25}N_2O_5PS_2$
20.	H	H	CH_3	nC_3H_7	188	$C_{17}H_{25}N_2O_5PS_2$
21.	Cl	H	Cl	nC_4H_9	182	$C_{18}H_{25}Cl_2N_2O_5PS_2$
22.	H	H	Cl	nC_4H_9	179	$C_{18}H_{26}ClN_2O_5PS_2$
23.	H	H	CH_3	nC_4H_9	199	$C_{19}H_{29}N_2O_5PS_2$

1. All the m.p.s were taken in open capillary tubes and are uncorrected, elemental analysis of the compounds were found satisfactory.
2. Yield of the compounds ranges between 50 to 80%.

Determination of acetylcholinesterase activity.

The method of Hestrin[13] as described by Colwick and Kaplan[14] was used to determine anti-AchE activity. Compounds were dissolved in water and used at a conc. of $3 \times 10^{-4} M$. A control containing equal volume of water was also run in parallel. Compound No. 3,4,6, 8,10,11,17&18 were tested but only three compounds (3,4 and 10) showed marginal inhibition.

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Saponins from *Randia dumetorum* Lamk. Fruit Pulp

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The fruit pulp of *Randia dumetorum* Lamk. commonly known as 'Mainphal' yields six saponins named as dumetoronin A,B,C,D,E and F and four free sugars. The structure of all the six saponins have been discussed. Three of the free sugars have also been identified.

RANDIA dumetorum Lamk. commonly known as 'Mainphal' in Hindi belongs to the family Rubiaceae. It is used in the Indian system of medicine as emetic, antidysenteric and as fish poison[1]. Recently, it has been found that it has antifertility property[2].

Vogtherr[3] was the first to isolate the saponin, m.p. 250° which on hydrolysis yielded a genin and two sugars of which the osazones melted at 166-167° and 176-77°. Later on Gedeon[4] isolated two saponins m.p. 260° and 289° and thought one to be the saponin and the other to be prosapogenin as both these products on hydrolysis yielded the same sapogenin, oleanolic acid.

In 1954, Chinese workers[5] isolated a saponin which contained glucose, fructose, and glucuronic acid in the ratio of 1 : 3 : 3. Later on, Varshney and Sannie[6] isolated a colourless saponin which on hydrolysis gave oleanolic acid, 1 mole of glucose, 1 mole of fructose, 1 mole of xylose and probably two moles of glucuronic acid.

In 1960 Atal *et al*[7]. isolated a saponin named, ursosaponin from the fruits of this plant which on hydrolysis gave ursolic acid. Recently, Dhar *et al*[8]. studied the bark of this plant and isolated two genins, randialic acid A (19-α-hydroxy ursolic acid) and randialic acid B (19-dehydro-ursolic acid).

In view of these conflicting reports a reinvestigation of *Randia dumetorum* Lamk. fruits was taken up.

The dried fruits obtained from the local market were broken into small pieces and the dry pulp was separated, powdered and defatted with light petroleum ether. The well defatted powder was exhaustively extracted with ethanol. The ethanolic extract on concentration and subsequent treatment and precipitation[9] gave a colourless powder which gave all the tests for saponin. The saponin on TLC showed eleven spots. These products were separated on a column of silica gel (cf. Table 1). The first spot corresponded to free genin and was identified as oleanolic acid by m.p., m.m.p. and comparison of IR. spectrum with that of an authentic sample. The middle six spots were identified as saponins while last four as free sugars.

TABLE 1

Length of column 75 cm 4 gm. Weight of substance 4 gm
Diameter of colum 2.5 cm Volume of each fraction 10 ml.
Weight of silicagel 170 gm.

Sr. No.	Fraction	Eluant	Substance
1.	1-5	$CHCl_3-CH_3-OH-H_2O$ (65 : 35 : 10)	Free genin (Oleanolic acid)
2.	6-18	-do-	Mixture of F, E and genin
3.	19-22	-do-	E
4.	23-24	-do-	Mixture of E and D
5.	25-30	-do-	D
6.	31-55	-do-	Midture of D and C
7.	56-59	-do-	D C and B
8.	60-66	-do-	B
9.	67-76	$CHCl_3-CH_3-OH-H_2O$ (65 : 35 : 10)	Mixture of B and A
10.	77-89	-do-	A
11.	90-92	(65 : 45 : 10)	A and free sugars
12.	93-100	90% Methanol	Free sugars

By rechromatography of the various mixtures, all the six products have been separated in pure form and all of them gave the tests for saponin. All the six saponins were obtained in the pure state and named as Dumetoronin A,B,C,D,E and F. The dumetoronin A,B,C and D were present almost in equal amounts while E and F were present in trace amounts. All the saponins were separately hydrolysed with $2N$ aqueous sulphuric acid and all of them gave oleanolic acid identified by mp, m.m.p. and comparison of IR spectrum with an authentic sample. The saponins gave difference in sugars identified by paper chromatography (cf. Table 2). This showed that all dumetoronins are the glycosides with the same aglycone (oleanolic acid) and have different sugars.

TABLE 2—SUGARS PRODUCED ON HYDROLYSIS OF SAPONINS

Saponins	Sugars produced on acid hydrolysis
Dumetoronin A & B	Glucuronic Acid, glucose, arabinose, xylose, rhamnose and unknown sugar*
Dumetoronin C & D	Glucose, arabinose, xylose, rhamnose and unknown sugar*
Dumetoronin E	Glucose, rhamnose and unknown sugar*
Dumetoronin F	Glucose and unknown sugar*

Dumetoronins A,B,C,D,E and F were separately refluxed with 5% sodium hydroxide for four hours. The reaction mixtures were neutralized with ion-exchange resin IR 120 (H^+) and then concentrated under reduced pressure. Examination of these products by TLC showed a single spot in each case which corresponded to the original saponins indicating that-COOH group was free in all the saponins and the sugars were attached at C-3 OH group.

The crude saponin mixture was methylated with diazomethane. The methyl esters formed were separated on a column of silica gel (cf. Table 3).

The methyl ester of different dumetoronins were identified by separately methylating the pure dumetoronin A,B,C,D,E and F.

The methyl esters of dumetoronin A,B,C,D,E and F were obtained in pure state which on acid hydrolysis gave sapogenins identified as methyl ester of oleanolic acid and the sugars as in the saponins. This confirmed that in all the above saponins the -COOH group is free and all the sugars are attached to C-3 hydroxyl group.

Dumetoronin D was methylated by dimethyl sulphoxide, silver oxide and methyl iodide. The partially methylated dumetoronin D thus obtained was subjected to two Purdie's[10] methylation, yielding fully methylated dumetoronin D. The fully methylated dumetoronin D on acid hydrolysis gave methyl ester of oleanolic acid

TABLE 3

Length of column 60 cm Weight of substance 2.5 gm
Diameter of column 2.5 cm Volume of each fraction 20 ml.
Weight of silica gel 150 gm.

No.	Fraction	Eluant		Substance
1.	1-4	$CHCl_3-CH_3OH$	(95 : 5)	Methyl easter of oleanolic acid
2.	5-7	-do-	-do-	Methyl ester of oleanolic acid and of F
3.	8-11	-do-	-do-	Methyl ester of F
4.	12-14	-do-	-do-	Methyl ester of F and E
5.	15-19	-do-	-do-	Methyl ester of E
6.	20-25	-do-	(90 : 10)	Methyl ester of E and D
7.	26-34	-do-	-do-	Methyl ester of D
8.	35-45	-do-	(80 : 20)	Methyl ester of D and C
9.	46-48	-do-	-do-	Methyl ester of C
10.	49-52	-do-	-do-	Blank
11.	53-59	-do-	(75 : 25)	Methyl ester of B
12.	60-67	-do-	-do-	Methyl ester of B and A
13.	68-76	-do-	(70 : 30)	Methyl ester of A
14.	77-85	Eluted with 90% Methanol		Free sugars and traces of Methyl ester of A

and six sugars, out of these four were identified by paper chromatography and GLC as 2,3,4,6-tetra-O-methyl-D-glucose, 2,3,4-tri-O-methyl-D-glucose, 2, 3, di-O-methyl-L-arabinose and 2, 4-di-O-methyl-D-xylose. The two other methyl sugars could not be identified.

The partial hydrolysis of dumetoronin A was carried out under varying conditions (cf. Table 4) and gave the following results.

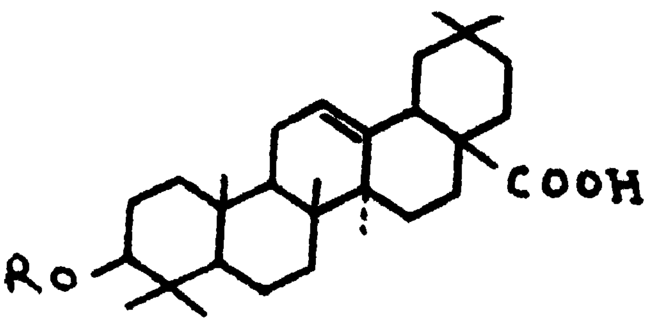
TABLE 4—PARTIAL HYDROLYSIS OF DUMETORONIN A

No.	Strength of acid	Time	Temperature	Products of hydrolysis
1.	0.1 N	1 hr.	60°	Prosapogenin, corresponding to dumetoronin B and glucose.
2.	0 2 N	½ hr.	95°	Dumetoronin B, one more prosapogenin, glucose and unknown sugar.
3.	0.5 N	1 hr.	95°	Prosapogenins, glucose, xylose, and traces of arabinose and unknown sugar.
4.	1 N	1 hr.	95°	Seven prosapogenins, glucose xylose, arabinose, and unknown sugar

These results show that dumetoronin A differs from dumetoronin B only by a glucose unit. This was further confirmed by enzymatic hydrolysis of dumetoronin A with β-glucosidase when only glucose was released and prosapogenin formed was identical with dumetoronin B. In the same manner dumetoronin B,C and D were partially hydrolysed with sulphuric acid. Dumetoronin D on hydrolysis with β-glucosidase gave glucose.

Some of the prosapogenins formed in the partial hydrolysis of dumetoronin A corresponded to the prosapogenins formed in the partial hydrolysis of dumetoronin B, C, and D indicating that all dumetoronins are interrelated.

On the basis of above results the following partial structures have been assigned to dumetoronin A,B,C,D,E and F.



Where R for Dumetoronin A and Dumetoronin B	Glucuronic acid, glucose, arabinose, xylose, rhamnose unknown sugar*
For Dumetoronin C and Dumetoronin D	Glucose, arabinose, xylose, rhamnose and unknown sugar*
For Dumetoronin E	Glucose, rhamnose and unknown sugar*
For Dumetoronin F	Glucose and unknown sugar*

Free Sugars : Free sugars obtained by column chromatography (cf. Table 1) by elution with 90% methanol were evaporated under reduced pressure to a syrup which on paper chromatography showed the presence of four sugars. But out of these four, three have been identified as sucrose, glucose and fructose by co-chromatography with authentic samples. The fourth one could not be identified due to paucity of material and seems to be a higher saccharide than sucrose. It had slow mobility (Rg. 0.43) than sucrose (Rg. 0.77) on Whatman filter paper No. 1 in n-butanol-pyridine-water (6 : 4 : 3) and on acid hydrolysis it gave glucose and fructose. It is also possible that there is present only the higher saccharide giving sucrose which partially gives glucose and fructose.

* It is the same unknown sugar in all saponins.

Experimental

TLC and column chromatography were carried outon silica gel. at NCL, Poona, Paper chromatography was carried out on Whatman No. 1 and 3 mm filter papers using the solvents (v/v) : (S_1) n-butanol-pyridine-water (6 : 4 : 3), (S_2) n-butanol-ethanol-water (4 : 1 : 5) and (S_3) butanone-water azeotrope (100 : 17). The solvent systems used for TLC and column chromatography were (A_1) chloroform-methanol-water (65:35:10), (A_2) chloroform-methanol-water (65:45:10), (B) benzene-acetone (6 : 1) and (C) chloroform-methanol (9 : 1).

The spray reagents used were (a) acetonic silver nitrate-ethanolic sodium hydroxide, (b) *p*-anisidine phosphate, (c) *p*-anisidine hydrochloride and (d) aniline hydrogen phthalate. GLC was done on AIMIL-NCL gas chromatograph using flame ionization detector and the column of 3% ECNSS-M on chromosorb-W. The purity of all saponins was checked by electrophoresis carried out on Whatman filter paper No. 1 using borate buffer (0.1 *M*) at 400 V for 4 hr. and stannic chloride was used as spraying reagent.

The deffatted pulp was exhaustively extracted with ethanol which on concentration yielded a brownish powder. This on subsequent treatment with various solvents and precipitation gave a colourless powder of saponin. This on TLC showed eleven spots, out of these six were identified as saponin, four as free sugars and one as free genin. The crude mixture of saponins on chromatography on a silica gel column (cf. table 1) gave six pure saponins named as dumetoronin A,B,C,D,E and F and a mixture of four free sugars.

The crude saponin mixture (2 *gm*) was twice methylated with diazomethane for 16 hr. at 5°. The methyl esters thus obtained were separated by column chromatography on silica gel (cf. Table 3).

Dumetoronin A : Dumetoronin A (400 mg) was hydrolysed with aqueous sulphuric acid (2*N*, 400 ml) by refluxing for 6 hr. and gave an acid genin identified as oleanolic acid (85 mg) m.p. 309-10°, methyl ester m.p. 196-98°, acetyl methyl ester m.p. 216-18° (cf. lit. oleanolic acid m.p. 310° methyl ester of oleanolic acid m.p., 198-200° and acetyl methyl ester of oleanolic acid m.p. 219-20°.

The hydrolysate of dumetoronin A was neutralized with freshly precipitated barium carbonate and deionised by passing through a column of ionexchange resins (Amberlite IRA 400 and IR 120 (H^+). The sugar solution obtained was concentrated under reduced pressure to a syrup. It was chromatographed on Whatman filter paper No. 1 in solvent S_1 and showed the presence of six sugars namely glucuronic acid, glucose, arabinose, xylose, rhamnose and an unknown sugar.

Dumetoronin A (50 mg) was refluxed with a 5% solution of sodium hydroxide in methanol-water (1:1) for 4 hr. It was recovered unchanged.

Dumetoronin A (50 mg) was methylated with diazomethane in the usual manner and gave the methyl ester of dumetoronin A(55 mg) m.p. 98° (decomp.). Dumetoronin A methyl ester (40 mg) was hydrolysed with aqueous sulphuric acid (2*N*, 50 ml) by refluxing for 6 hr. and yielded methyl ester of oleanolic acid (10 mg). The hydrolysate after neutralization and deionisation showed the presence of six sugars identified as glucuronic acid, glucose, arabinose, xylose, rhamnose and unknown sugar.

Dumetoronin A (20 mg) was dissolved in sodium acetate buffer (10 ml, *p*H 5.0) and a portion of β-glucosidase solution (30 mg. in 10 ml. water) was added to it. The mixture was then sealed in a glass tube and kept at 38°. The tube was cut open after 24 hr. and the solution was concentrated to a syrup. The syrup was examined by TLC and by paper chromatography and showed the presence of glucose and dumetoronin B (Rf. 0.41 in solvent A_1).

The partial hydrolysis of dumetoronin A was carried out with different strengths of sulphuric acid under varying conditions as described in Table 4.

Dumetoronin D: Dumetoronin D had m.p. 259-61° (decomp.) and Rf 0-71 in solvent A_1. 400 mg of it was hydrolysed with aqueous sulphuric acid (2*N*, 200 ml) by refluxing for 6 hr, gave an acid genin m.p. 309-10° identified as oleanolic acid (155 mg). The hydrolysate on usual treatment gave five sugars namely glucose, arabinose, xylose, rhamnose and an unknown sugar. Dumetoronin D (50 mg) could not be hydrolysed with a 5% solution of sodium hydroxide in 4 hr.

Dumetoronin D(50 mg) was methylated with diazomethane and gave methyl ester of dumetoronin D, m.p. 152-55°. Dumetoronin D methyl ester (40 mg) was hydrolysed with 2*N* aqueous sulphuric acid in the usual manner and gave methyl ester of oleanolic acid (20 mg) as genin and five sugars, namely glucose, arabinose, xylose, rhamnose and the same unknown sugar as in the case of dumetoronin A.

Dumetoronin D (150 mg) was permethylated with dimethyl sulphoxide (10 ml), methyl iodide (5 ml) and silver oxide (300 mg) under anhydrous conditions for 48 hr. and then by Purdie's method. Complete methylation was checked by IR spectrum. The fully methylated dumetoronin D was hydrolysed with 2*N* sulphuric acid in the usual manner and the methylated sugars thus obtained were identified by co-chromatography and GLC and showed the presence of six methylated sugars. Out of which four were identified as 2,3,4,6-tetra-O-methyl-D-glucose, 2,3,4-tri-O-methyl-D-glucose, 2,4-di-O-methyl-D-xylose and 2,3,-di-O-methyl-L-arabinose by Rg and RTg values.

Dumetoronin E: It had m.p. 301-3°, Rf 0.85 in solvent A_1 and was sparingly soluble in water. On hydrolysis it gave, oleanolic acid and glucose, rhamnose and the same unknown sugar.

Dumetoronin F: It had m.p. 306-6°, Rf. 0.89 in solvent A_1 and was sparingly soluble in water. On hydrolysis it gave oleanolic acid and glucose and the same unknown sugar.

The unknown sugar was found to be the same in all dumetoronin A, B, C, D, E and F and had Rf 0.87 in solvent S_1.

Free sugars: The sugar mixture obtained by eluting the column with 90% methanol (cf. Table 1), was chromatographed on Whatman filter paper No. 1 in solvent S_1 showed the presence of four sugars which was separated quantitatively by paper chromatography on Whatman 3 mm filter papers in solvent S_1. It gave four fractions. Fractions (I), (II) and (III) were identified as fructose (Rg 1.1), glucose and sucrose (Rg 0.77) respectively by co-chromatography with authentic samples while fraction (IV) (Rg 0.43) on acid hydrolysis gave glucose and fructose, identified by paper chromatography. Further study of this sugar could not be done due to paucity of the material.

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Synthesis of 2-Amino Thiazole Derivatives

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Synthesis of 2-amino thiazole derivatives and their effect on blood sugar are studied.

FROM the therapeutic point of view thiazole derivatives are of considerable interest, since their utility in the treatment of diseases has been firmly established[1,2]. Thiazole derivatives contain thiourea moiety and, therefore, like urea derivatives can possibly act as hypo/hyper glycemic agents[3,4]. In view of these possibilities, variously substituted thiazole derivatives were synthesised (Table 1) and some of them were tested for their biological properties.

4(Substituted phenyl)-2-amino thiazoles were prepared by Dodson and Kings' method and also by Hantzsch thiazole synthesis. The acetophenones and 2-haloketones required for the above synthesis were prepared by Fries migration and Fridel-Craft reaction respectively. 5-Carbethoxy-4-(substituted)-2-amino-thiazoles were prepared by Dodson and Kings' method. The β-ketoesters required for the preparation of the above thiazole derivatives were prepared by the methods

TABLE 1 — MELTING POINTS AND ELEMENTAL ANALYSIS OF 2-AMINO THIAZOLES

No.	2-Amino-thiazole (Only 4-phenyl substituent is given)	M.P °C	Yield %	Formula	Carbon %		Hydrogen %	
					Calcd.	Found	Calcd.	Found
1.	4-(2'-Hydroxy-4'-chloro-phenyl),	183-5 (220)	40	$C_9H_7N_2ClOS$	47.68	47.75	3.09	2.96
2.	4-(2'-Hydroxy-4'-bromo-phenyl)-	197 (254)	35	$C_9H_7N_2BrOS$	39.85	39.96	2.58	2.48
3.	4-(2'-Hydroxy-4'-iodo-phenyl)-	216 (285)	40	$C_9H_7N_2IOS$	33.96	34.36	2.20	1.50
4.	4-(2'-Chloro-4'-hydroxy-phenyl)-	148 (130)	20	$C_9H_7N_2ClOS$	47.85	46.99	3.09	2.14
5.	4-(3',4'-Dichlorophenyl)-	153 (250)	70	$C_9H_6N_2Cl_2S$	44.08	44.13	2.44	2.40
6.	4-(2',5'-Dichlorophenyl)-	169 (164)	70	$C_9H_6N_2Cl_2S$	44.08	44.14	2.44	3.10
7.	4-(2'-Chloro-5'-methyl-phenyl)-	120 (139)	70	$C_{10}H_9N_2ClS$	53.46	53.49	4.02	4.36
8.	4-(2'-Bromo-5'-methyl-phenyl)-	95 (151)	60	$C_{10}H_9N_2BrS$	44.67	44.70	3.34	3.55
9.	5-Carbethoxy-4-(2'-methyl phenyl)-	175	30	$C_{13}H_{14}N_2O_2S$	59.54	59.32	5.34	4.70
10.	5-Carbethoxy-4-(3'-methyl -phenyl)-	173	30	$C_{13}H_{14}N_2O_2S$	59.54	59.04	5.34	5.52
11.	5-Carbethoxy-4-(4'-methyl -phenyl)-	134	40	$C_{13}H_{14}N_2O_2S$	59.54	59.17	5.34	4.98
12.	5-Carbethoxy-4-(4'-nitro-phenyl)-	225	60	$C_{12}H_{11}N_3O_4S$	49.15	49.99	3.75	2.82
13.	5-Carbethoxy-4-(2-furyl)-	137	30	$C_{10}H_{10}N_2O_3S$	50.42	50.14	4.20	2.55
14.	5-Carbethoxy-4-(2-thienyl)	165	30	$C_{10}H_{10}N_2O_2S_2$	47.25	46.84	3.39	2.80

The bracket figures represent the melting points of their hydroiodides (No. 1 to 4) and hydrochlorides (5 to 8).

described by Straley and Adams[5] while in literature these are synthesised by Claisen condensation.

The following acetophenones, 2-haloketones and β-keto esters were used in this work :

1. 2′-Hydroxy-4′-chloro acetophenone.
2. 2′-Hydroxy-4′-bromo acetophenone.
3. 2′-Hydroxy-4′-hydroxy acetophenone.
4. 2′-Chloro-4′-hydroxy acetophenone.
5. 2,3′,4′-Trichloro acetophenone.
6. 2,2′,5′-Trichloro acetophenone.
7. 2,2′-Dichloro-5′-methyl acetophenone.
8. 2-Chloro-2′-Bromo-5′-methyl acetophenone.
9. Ethyl-(*o*-toluoyl)-acetate.
10. Ethyl-(*m*-toluoyl)-acetate.
11. Ethyl-(*p*-toluoyl)-acetate.
12. Ethyl-(*p*-nitro benzoyl)-acetate.
13. Ethyl-(2-furoyl)-acetate.
14. Ethyl-(2-thenoyl)-acetate.

4-(Substituted phenyl)-2-aminothiazoles were converted into their sulpha derivatives by treating them with *p*-acetamido-benzene sulphonyl chloride and subsequent hydrolysis (Table 2).

2-Amino thiazoles (compound No. 5 and 6) are found to be identical to those reported in literature[6,7]. The structures of these 2-amino thiazoles were confirmed on the basis of their melting points and elemental analysis.

TABLE 2—MELTING POINTS AND ELEMENTAL ANALYSIS OF 2-SULPHANILAMIDO THIAZOLES

No.	2-Sulphanilamido thiazole (only 4-phenyl substitutent is given)	M.P. °C	Molecular Formula	Carbon %		Hydrogen %	
				Calcd.	Found	Calcd.	Found
1.	4-(2′-Hydroxy-4′-chloro-phenyl)-	175	$C_{15}H_{12}N_3ClO_3S_2$	47.19	45.90	3.19	4.52
2.	4-(2′-Hydroxy-4′-bromo-phenyl)-	184	$C_{15}H_{12}N_3BrO_3S_2$	44.68	44.09	3.12	2.56
3.	4-(3′,4′-Dichloro phenyl)-	158	$C_{15}H_{11}N_3Cl_2O_2S_2$	45.00	44.77	2.75	3.80
4.	4-(2′,5′-Dichlorophenyl)-	173	$C_{15}H_{11}N_3Cl_2O_2S_2$	45.00	45.32	2.75	2.86
5.	4-(2′-Chloro-5′-methyl-phenyl)-	95	$C_{16}H_{14}N_3ClO_2S_2$	50.59	50.82	3.68	2.48
6.	4-(2′-Bromo-5′-methyl-phenyl)-	85	$C_{16}H_{14}N_3BrO_2S_2$	45.28	44.89	3.30	2.80

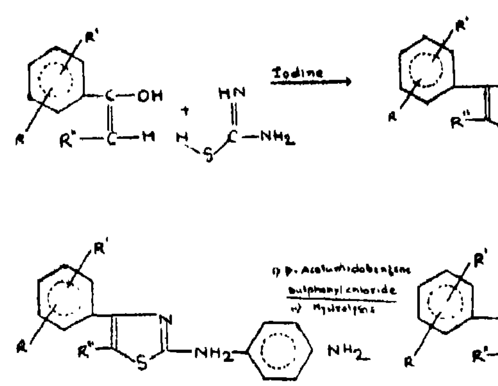


Fig. 1A

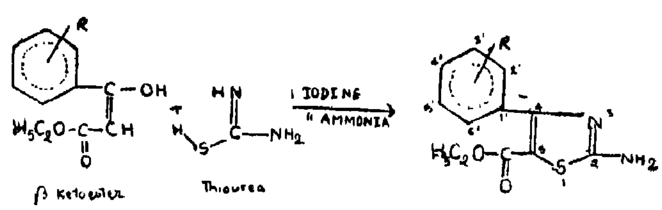


Fig. 1C

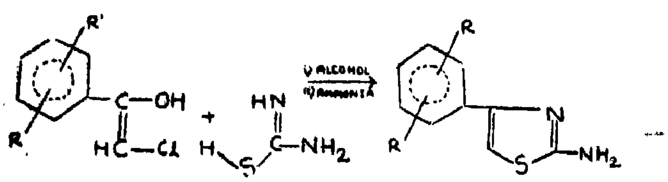


Fig. 1B

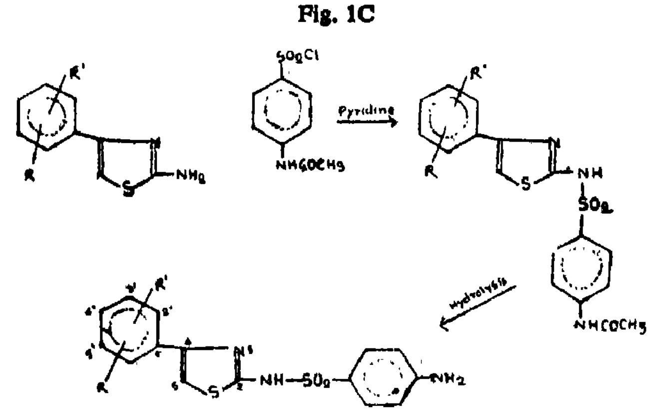


Fig. 1D

Hypo/hyperglycemic activity :

2-Amino thiazoles prepared in this work were tested for their hypo/hyper glycemic activity. The activity was tested in normal rats (average weight 200 gm). They were divided into groups of seven and fed orally with test compounds (150 mg/kg) as solution in 5% tragacanth. Seven rats were kept as control. After every hour blood samples were drawn from tail veins for the measurements of glucose content. Changes in the glucose content in the blood of the tested rats were compared with that of the control groups at intervals of 1,2,4 and 48 hours in each case. The data of the *in vivo* activity tests of the above compounds are given (Table 3).

TABLE 3—HYPO/HYPERGLYCEMIC ACTIVITY OF 2-AMINO THIAZOLES

No.	2-Amino-thiazole (only 4-substituent is given)	Percentage increase (+) or decrease (−) of blooa glucose effected by compound (b) 1 hr.	2 hrs.	4 hrs.	Results
1.	4-(2′-Hydroxy-4′-chlorophenyl)-	+13	+10	−3	hyperglycemic
2.	4-(2′-Hydroxy-4′-iodophenyl)-	+ 6	+ 5	−2	inactive
3.	4-(2′-Chloro-4′-hydroxyphenyl)-	− 5	− 4	−4	inactive
4.	4-(3′,4′-Dichlorophenyl)-	− 4	− 5	−12	inactive
5.	4-(2′,5′-Dichlorophenyl)-	+ 6	+ 6	+5	inactive
6.	5-Carbethoxy-4-(2′-methylphenyl)-	+ 3	+ 3	+16	hyperglycemic
7.	5-Carbethoxy-4-(4′-methylphenyl)-	+18	+31	+52	hyperglycemic
8.	5-Carbethoxy-4-(4′-nitrophenyl)-	−2	−4	zero	inactive
9.	5-Carbethoxy-4-(2′-thienyl)-	−4	−2	zero	inactive

(b): Results and expressed as the percentage difference in mg. percent between the mean change in control treated groups after a drug dose of 150 mg/kg.

A compound is considered hypoglycemically active if it produces 30% decrease in blood glucose and hyperglycemically active if it produces 10% increase in blood glucose.

$$\text{Percentage change} = \frac{\triangle T - \triangle C}{\text{Control glucose value at that hour}}$$

$\triangle T$ = change of blood glucose from zero time for treated groups.

$\triangle C$ = change of blood glucose from zero time for control groups.

Experimental

Experiment No. 1.

Preparation of 4-(substituted phenyl)-2-amino-thiazoles : Dodson and Kings' method : (Fig. 1 A).

A mixture of acetophenone (0.01 mole), thiourea (0.02 mole) and iodine (0.01 mole) was heated on a steam bath for ten hours. The reaction mixture was cooled and repeatedly washed with ether to remove excess of iodine and unreacted acetophenone. It was then extracted with boiling water and filtered hot to remove solid impurities. The filtrate on cooling gave a reddish brown solid, which upon crystallisation from aqueous ethanol gave needles.

The hydroiodide obtained above was dissolved in water and neutralised with concentrated ammonia solution when a yellow coloured free base was obtained. It was then crystallised from ethanol.

Hantzsch thiazole synthesis : (Fig. 1 B).

A mixture of 2-halo ketone (0.01 mole), thiourea (0.013 mole) and alcohol (10 ml) was refluxed for one and half hours. It was then cooled. The solid crystalline hydrochloride thus separated was filtered and washed with ether to remove unreacted ketone. It was then dried and crystallised from aqueous ethanol.

The hydrochloride obtained above was boiled with water and ammonium hydroxide solution. The solid thus obtained was filtered and washed with water. Crystallisation from 95% ethanol gave fine crystal of 2-aminothiazole.

Experiment No. 2 : (Fig. 1C).

Preparation of 5-(carbethoxy)-4-(substituted)-2-amino-thiazoles.

A mixture of β-keto ester (0.05 mole), thiourea (0.1 mole) and iodine (0.05 mole) was heated on a steam bath for sixty hours. The reaction mixture was cooled and extracted with ether to remove unreacted β-keto ester and iodine. The residue was extracted with boiling water. On cooling, the hydroiodide was separated. It was neutralised by ammonia solution to get free amine. The solid thus obtained was filtered

and washed with ice cold water. Crystallisation from aqueous ethanol gave silky needles.

Experiment No. 3 :

Preparation of sulphanylamido thiazole : (Fig. 1 D).

A solution of 2-amino thiazole (0.015 mole) in dry pyridine (15 ml) was treated in portions with freshly prepared *p*-acetamidobenzene sulphonyl chloride (3 g). The reaction mixture was heated on a water bath for half an hour and then kept at room temperature for 48 hours. It was poured over crushed ice containing little sulphuric acid. The precipitated solid was filtered and washed with water. It was crystallised from 50% ethanol.

The acetyl sulphanylamido thiazole (1 g) obtained above was boiled with dilute hydrochloric acid (25 ml) and ethanol (5 ml) for half an hour. The reaction mixture was filtered hot and diluted with water. The sulphanylamido thiazole thus obtained was crystallised from aqueous ethanol.

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Thermogravimetry of Reclaimed Rubber Compounds

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Thermogravimetric analyses were carried out for reclaimed rubber and its compounds under different perspectives. Study on degradation characteristics was the principal object in the present series of experiments.

THERMAL analysis finds frequent use in the investigations of the influence of various factors on the thermogram characteristics of different elastomer systems[1,2]. Some results on differential thermal analysis (DTA) of reclaimed rubber compounds have been reported earlier[3,4,5]. The present communication deals with the thermogravimetric (TGA) studies on (a) compounds based separately on reclaimed rubber, natural rubber (NR) and reclaim-NR blend, (b) two different reclaims, and (c) effect of (i) sulphur, (ii) zinc oxide, and (iii) accelerator in a reclaim compound.

The TGA studies were carried out in a TGA apparatus fabricated in our laboratory. Temperature calibration corresponding to weight loss for the whole temperature range of interest was made by using known systems.

The recipe of the compounds [high-sulphur, containing the limiting proportion of sulphur (50 parts)[6,7]] is shown in Table 1 and their TGA thermograms in Figure 1. Curves I and III represent compounds based solely on natural rubber and reclaim respectively, whereas curve II stands for the compound based on their blend (ratio of hydrocarbon content=50 : 50). Among these three systems some identity is observed upto the temperature region of 200°, no weight loss being exhibited so long. Above this temperature zone each of the systems starts losing weight, the rates of loss varying in some extent from each other in the three cases. These present rates break above 250° and new rates are observed for all these systems, and found to follow parallel relations. Around 350°, weight loss starts at much faster rates as compared to the previous rates. Also the differences among the rates of the three systems at this stage are significantly greater than those noted previously. So far as this last section of these TGA curves are concerned, the difference between the rates of the NR-based and the reclaim-NR-blend-based compounds is, to a considerable extent, greater than that between the rates of compounds based on reclaim-NR blend and reclaim respectively. For all the three systems a tendency in the change of the rate of weight loss is observed above 400°.

TABLE 1

Formulation of Compounds* (parts by weight) analyzed by TGA

	I	II	III
Smoked sheet	100.0	50.0	–
Reclaim	–	100.00	200.0
Stearic acid	1.0	1.0	1.0
Zinc oxide	5.0	5.0	5.0
BA**	1.0	1.0	1.0
Sulphur	50.0	50.0	50.0

* The reclaim contains about 50% of rubber hydrocarbon. Therefore, the proportion of reclaim used is twice that of smoked sheet to be substituted.

** Butyraldehyde aniline.

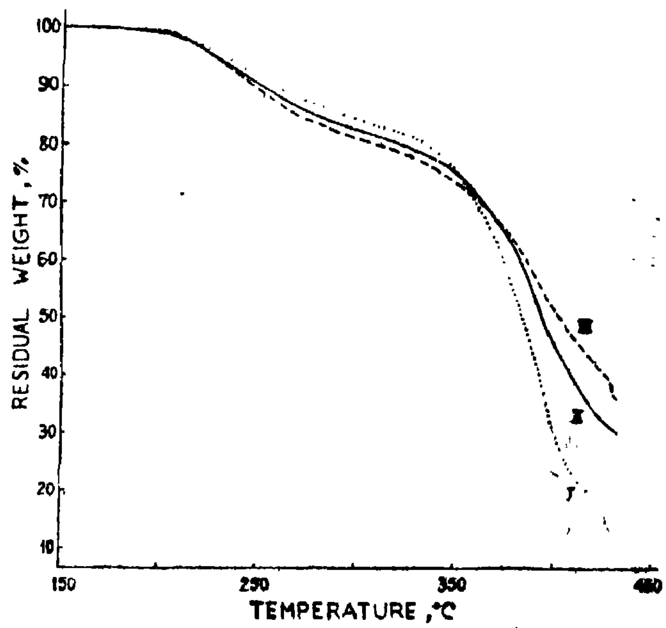


Fig. 1. : TGA curves for compounds based on natural rubber, natural rubber—reclaim blend and reclaim.

All these reveal the diminution in the tendency of degradation of natural rubber by incorporation of reclaim – a notable beneficial effect of reclaim for practical compounds and further supported in the DTA studies*.

Two different reclaims (as manufactured by two different manufacturers) were compared by TGA. The specifications of the pair of reclaims are shown in Table 2 and their TGA thermograms in Figure 2. Curves marked as reclaim A and reclaim B represent the two reclaims. From these two systems it is revealed that upto the temperature region around 250° neither of the reclaims exhibit any loss in weight. Above this temperature zone both the systems lose weight gradually, the rate of loss being higher for one reclaim (reclaim A) than that for the other one (reclaim B). Both the reclaims show at temperatures above 350° their weight loss at rates much different from and higher than the previous rates, but above 350° at initial stage the weiht loss for reclaim B proceeds at a higher rate than that for reclaim A and ultimately almost overlap.

TABLE 2—COMMERCIAL DATA SPECIFYING THE RECLAIMS.

	Ash	%Acetone extract, %	Carbon Black, %	Rubber Hydrocarbon by difference ; %
Reclaim A (WTR 100)	10±2	14±4	22±4	Not less than 50
Reclaim B (WTS)	5–8	14–18	22–25	52–55

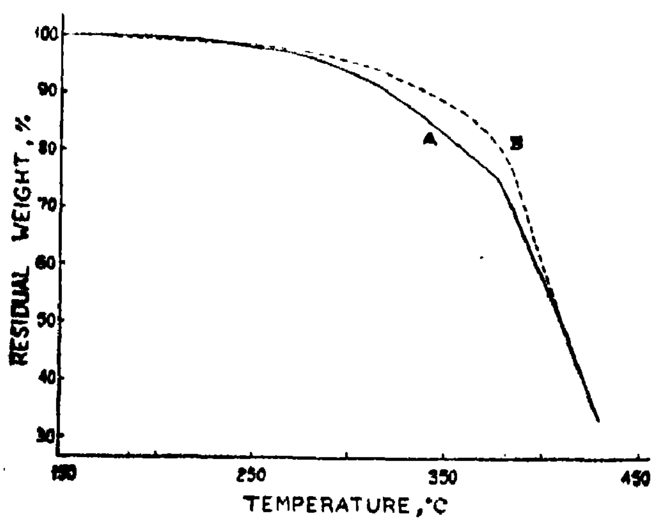


Fig. 2. : TGA curves of a pair of reclaims.

The above pair of reclaims (A and B) were also compared by DTA. The DTA thermograms are shown in Figure 3, where curves marked as reclaim A and reclaim B represent the two reclaims. It is found that the peak area and peak height of reclaim A is appreciably greater than those of reclaim B. Whereas initiation temperature of reclaim A is lower than that of the other, their peak temperatures are also somewhat different. On the other hand, slope of reclaim A is, to a considerable extent, higher than that of reclaim B and for both the reclaims some peaks are present in the high-temperature regions although in varying prominences.

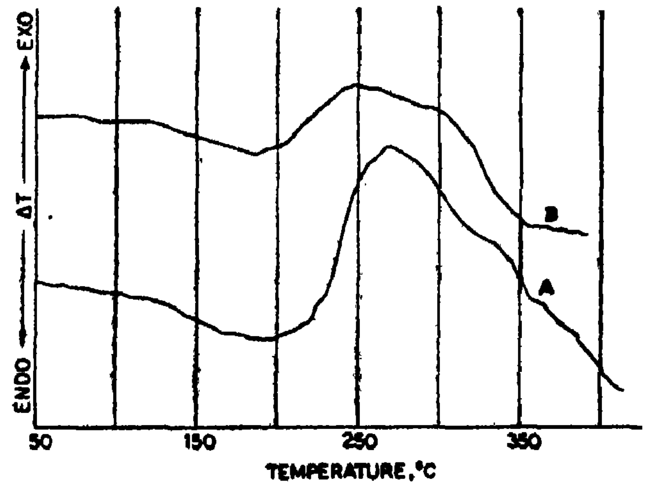


Fig. 3. : DTA curves of the pair of reclaims.

These studies indicated that the reclaim A had a much more affinity towards degradation than the reclaim B and hence the former contained more of natural rubber, and the latter more of styrene-butadiene rubber, predictable from the relative characteristics of these polymers[8].

Effect of Sulphur :

Table 3 represents the recipes of the compounds whose TGA thermograms are shown in Figure 4. Curves I and II represent respectively the high– and the low– sulphur compounds. Upto the temperature region around 200° practically no weight loss takes place for

TABLE 3

Formulation of Compounds* (parts by weight) analysed by TGA

	I	II
Reclaim	100.0	100.0
Stearic Acid	0.5	0.5
Zinc Oxide	2.5	2.5
TMTD**	0.5	0.5
Sulphur	25.0	1.5

* Formulations are based on 50% hydrocarbon content of reclaim.

** Tetramethylthiuram disulphide.

any of these systems. But in both cases weight loss is initiated above that temperature zone. The rate of loss in case of the high-sulphur compound is, however, muchhigher than that for the low-sulphur one. Above 250° a break in such rates is found in both the compounds with more prominence in the high-sulphur one, allowing new rates to follow. Further change in the rates of weight loss occurs above 350° for both the systems and the rates of each of the two at this stage are appreciably greater than the previous rates of the corresponding systems. In the high-sulphur compound the rate of loss once more tends to change above 400°.

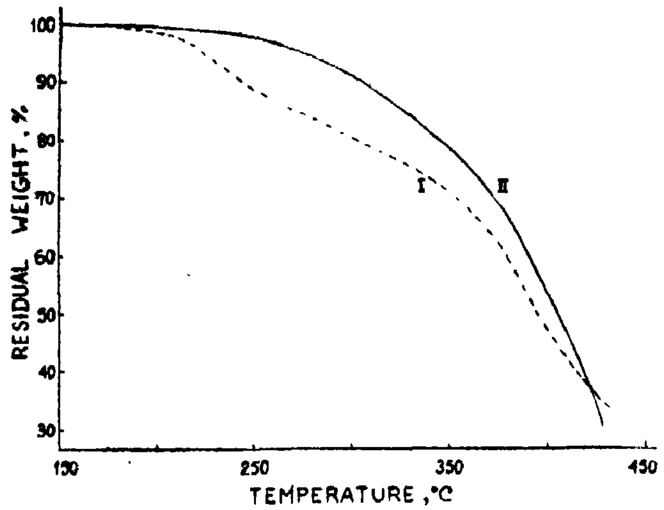


Fig. 4. : TGA curves of high— and low— sulphur compounds based on reclaim.

All these show, in general, the diminution in the affinity towards degradation with increasing sulphur content.

Effect of Zinc Oxide :

The recipes of the compounds are shown in Table 4, their TGA thermograms being shown in Figure 5. Curves a and b represent respectively the compounds in absence and in presence of zinc oxide. Both the systems indicate, beside little differences at different temperature zones, similar characteristics regarding the rates of weight loss.

TABLE 4

Formulation of Compounds* (parts by weight) analysed by TGA

	A	B
Reclaim	100.0	100.0
Stearic acid	0.5	0.5
Zinc oxide	—	2.5
BA	0.5	0.5
Sulphur	25.0	25.0

* Formulations are based on 50% hydrocarbon content of reclaim.

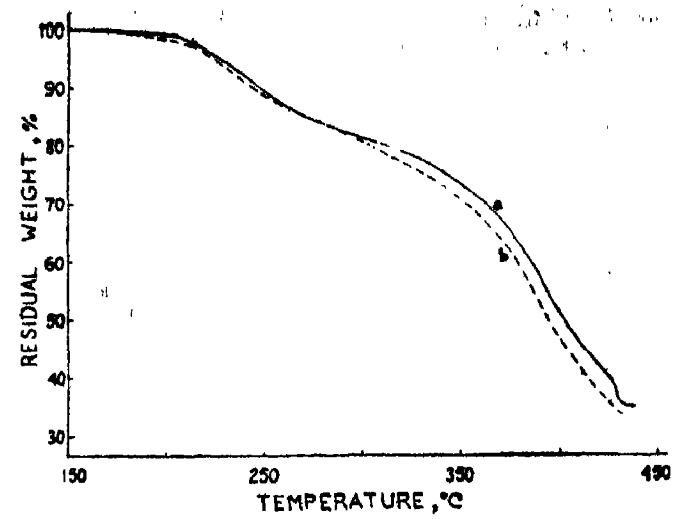


Fig. 5. : TGA curves of reclaim compounds with and without Zinc oxide.

Thus the incorporation of zinc oxide in a high-sulphur compound did not show any effect towards its thermal stability, as also supported by DTA studies[4].

Effect of Accelerator :

Table 5 displays the recipes of the compounds, whose TGA thermograms are shown in Figure 6. Curves a and b represent respectively the compounds with two different types of accelerators, BA and TMTD. At different temperature zones some differences were observed, otherwise characteristics exhibited were similar for both the systems. In both cases loss of weight practically starts only above the temperature region around 200°. Above 250° there is a break in the rate of weight loss. This break is, however, more prominent in the BA-containing compound than in the one containing TMTD. For both the systems the rate of weight loss significantly changes above 350° and these new rates

TABLE 5

Formulation of Compounds* (parts by weight) analysed by TGA

	a	b
Reclaim	100.0	100.0
Stearic acid	0.5	0.5
Zinc Oxide	2.5	2.5
BA	0.5	—
TMTD	—	0.5
Sulphur	25.0	25.0

* Formulations are based on 50% hydrocarbon content of reclaim.

are found to proceed almost in parallel. Above 400° a further tendency of the change of rate is observed.

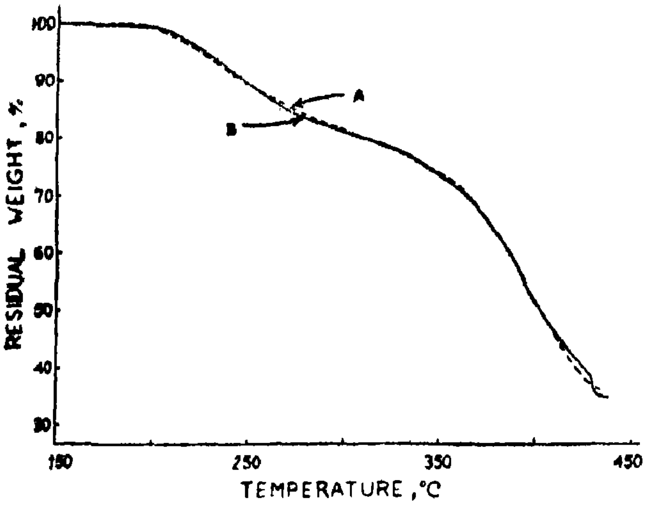


Fig. 6. : TGA curves of reclaim compounds with different accelerators.

This reveals, in general, that irrespective of the type of accelerator used high-sulphur reclaim compounds exhibit a similar trend towards their thermal stability characteristics.

Acknowledgement

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Notes

Rhenium XII*. A Polarographic Study of the Complex Dioxobis (ethylenediamine) rhenium(V) Chloride

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RHENIUM exhibits a widely different oxidation states and offers an interesting field for investigation by polarographic method. Various workers[1–9] have studied the polarographic reduction of perrhenate in a variety of supporting electrolytes, but studies with rhenium complexes as the starting material are very rare[7–10]. One of us has previously investigated[10] the polarographic reduction of $[ReO_2py_4]Cl$ and found that under the experimental conditions the complex is reversibly reduced to a Re(IV) complex containing two pyridine molecules.

The only well known ethylenediamine complex of rhenium is $[ReO_2en_2]Cl$ and is formed by the oxidation of $K_2[ReCl_6]$ by air in the presence of ethylenediamine[11]. In the lower valency states the ethylenediamine complexes of rhenium are rare and as such it is interesting to study the polarographic reduction of $[ReO_2en_2]Cl$.

Experimental

All the chemicals used were of BDH Analar grade or E. Merck's GR quality. Potassium perrhenate used was of Degussa (West Germany). $K_2[ReCl_6]$ and $[ReO_2en_2]Cl$ were prepared according to known procedures[11,12]. Distilled water redistilled in an all glass apparatus with a little $KMnO_4$ and KOH, was used for preparing all the solutions.

Polarograms were recorded in a Czechoslovak pen-recording polarograph (Polarograph, type LP 7 in workingc onjunction with EZ 7Electronic compensation Line Recorder, Laboratory Instruments, National Corporation, Praha) with a dropping mercury electrode and an external saturated calomel electrode. At a mercury height of 30 cm the capillary of the dropping mercury electrode had the following characteristics: $m = 1.79$ mg/sec and $t = 5.21$ sec/drop (in open circuit and in 0.2*M* KCL solution containing 0.005% gelatin).

The *p*H of the solutions was measured by a Digital *p*H Meter (p^H 822, Electronic Corporation of India Limited).

The solutions for polarography were made by mixing stock solutions of $[ReO_2en_2]Cl$, potassium chloride and gelatin and diluting to a known volume. The strengths of potassium chloride and gelatin were kept constant throughout (0.2M and 0.005% respectively). Pure hydrogen was passed through the solutions to remove dissolved oxygen. For recording the polarograms in the presence of ethylenediamine pure hydrogen was first passed through a bubbler containing the same electrolyte of identical concentration and then through the test solution.

Results and Discussion

The polarogram of $[ReO_2en_2]Cl$ in 0.2 *M* potassium chloride gave a well defined cathodic reduction wave with a half-wave potential of -1.150 V vs SCE at 28°. The plots of i_d vs $(h_{eff})^{\frac{1}{2}}$ and i_d vs C (where $h_{eff} = h - 3.1/m^{1/3}\, t^{1/3}$ and C = concentration of the complex) were found to be linear indicating that the reduction was diffusion-controlled. The plot of E_{de} vs log $(i_d - i)/i$ was found to be linear with a slope of 0.063, which is almost equal to the expected value of 0.060 for $n = 1$. Thus, under the experimental conditions Re(V) in $[ReO_2en_2]Cl$ is reversibly reduced to Re(IV).

TABLE 1—VARIATION OF HALF-WAVE POTENTIAL WITH INCREASING CONCENTRATION OF ETHYLENEDIAMINE

Concentration of $[ReO_2en_2]Cl$, 0.98×10^{-3} *M*
Temperature 28°

Concentration of ethylenediamine $M \times 10^3$	$E_{\frac{1}{2}}$ V vs SCE	*p*H of the solution
—	−1.150	5.95
4.5	−1.162	10.14
7.1	−1.172	10.52
12.2	−1.183	
17.3	−1.190	
22.4	−1.195	10.85
27.5	−1.200	
53.0	−1.210	11.06

The $E_{\frac{1}{2}}$ values were found to shift towards more negative direction with increasing ethylenediamine concentration (Table 1). For determining the composition of the complex in the reduced state, the half-wave potentials of the electrolytes were measured as a function of the concentration of ethylenediamine which was progressively increased. The half-wave potentials when plotted against the logarithm of the

* Part XI. M. C. CHAKRAVORTI and C. K. DAS, *Inorg. Chim. Acta.*, 1976, 19, 249.
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concentration of the corresponding ethylenediamine gave a straight line with a slope of 0.049. From the following equation[13]

$$E_{\frac{1}{2}}=E^{\circ}+\frac{0.060}{n}\log\frac{K_{ox}}{K_{red}}-\frac{0.060}{n}(p\text{-}q)\log C$$

the slope of the curve is $\frac{0.060}{n}(p\text{-}q)$. Putting the value of n as one and p, the number of molecules of ethylenediamine in dioxobis(ethylenediamine)rhenium(V) chloride, as two, the value of q (the number of molecules of ethylenediamine in the new complex) comes to 1.19, which when rounded up becomes equal to one. The most probable composition of the Re(IV) complex appears to be $ReenCl_4$. Though this particular compound has not been reported, a similar compound $ReenI_4$ has been isolated by us[14]. A large number of analogous compounds with other ligands are well known[15], viz. $ReCl_4L_2$ (where L = py, ½ bipy, trialkyl phosphine, etc.).

In passing from the minimum ($4.5\times10^{-3}M$) to the maximum ($5.3\times10^{-2}M$) concentration of ethylenediamine added, the *p*H of the medium increased by about one unit (Table 1). Polarograms of $[ReO_2en_2]Cl$ were recorded at different *p*H values (upto a *p*H of 11) by adding different volumes of caustic soda solution and it was observed that there was no change in $E_{\frac{1}{2}}$. It can thus be assumed that the change in $E_{\frac{1}{2}}$ with the increasing concentration of ethylenediamine was solely due to the variation in the concentration of ligand ethylenediamine.

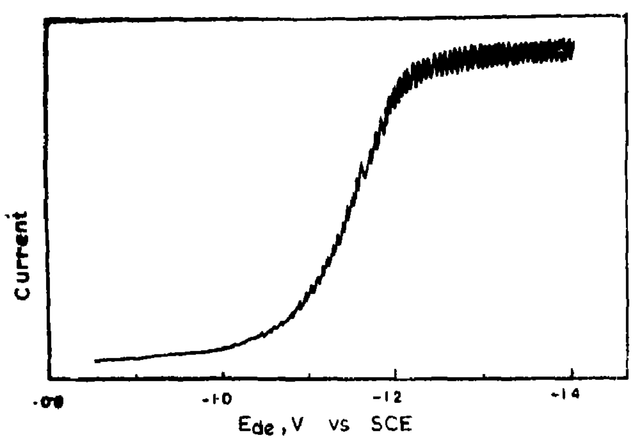


Fig. 1. Polarogram of $[ReO_2en_2]Cl$ ($5.05\times10^{-4}M$) in 0.2*M* KCl.

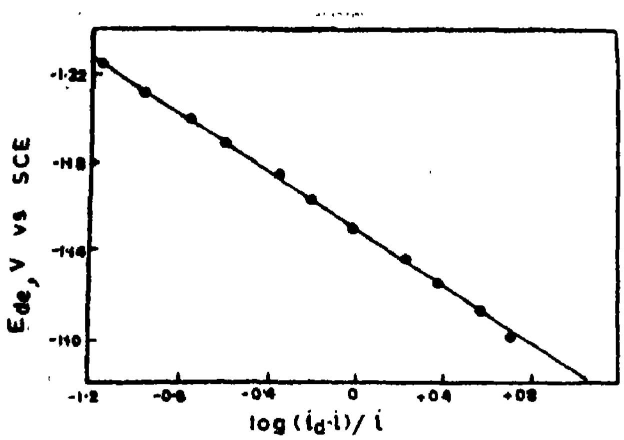


Fig. 2. Plot of E_{de} vs log $(i_d$-i)/i

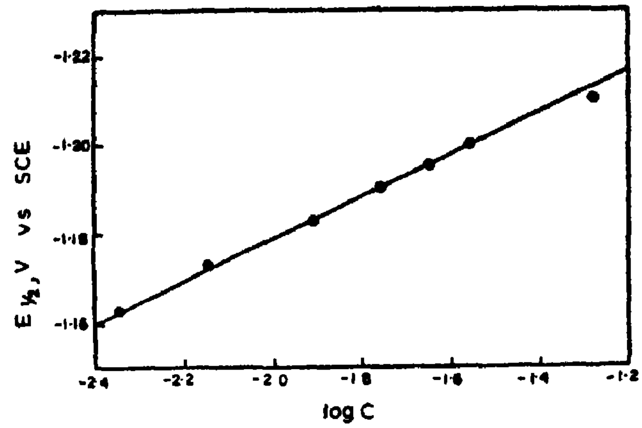


Fig. 3. Plot of $E_{\frac{1}{2}}$ vs logarithm of concentration of ethylenediamine.

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Polarographic Study of the Composition and Stability Constant of Citrate Complex of Mn(II)

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POLAROGRAPHIC reduction of Mn(II) in various aqueous and non-aqueous non-complexing media has been studied by a number of workers[1-5]. Gaur et al.[6,7] have undertaken a polarographic study of formate, sulphate and salicylate complexes of Mn(II). However, a polarographic study of the composition and stability constant of citrate complex is lacking. With this aim in view, it was thought worthwhile to uudertake this study.

Experimental

All the chemicals used were of A.R., B.D.H. or E.Merck G.R. grade. Stock solution of Mn(II) was prepared by dissolving $MnCl_2$ in conductivity water and its concentration was kept at $1.0 \times 10^{-3} M$. Potassium citrate solution was used as the source of citrate ions. KNO_3 was used to maintain constant ionic strength ($\mu = 1.0$).

A manual polarograph (Toshniwal, CLO2) in conjunction with Toshniwal polyflex galvanometer (PL 50) was used to obtain current-potential curves. All the measurements were made at $25 \pm 0.1°$. Triton X-100 (0.002%) was used as a maximum suppressor. Purified hydrogen was passed through the solution for removing dissolved oxygen. The d.m.e., used in conjunction with S.C.E., had the following characteristics :

$$h_{corr.} = 37.61 \text{ cm}$$

$$m^{2/3} t^{1/6} = 3.016 \text{ mg}^{2/3} \text{ sec}^{-1/2} \text{ (in } 0.1M \text{ KNO}_3\text{, open circuit).}$$

Results and Discussion

Mn(II) gives a single diffusion controlled reduction wave at different concentrations of the citrate ions. The $E_{1/2}$ values are shifted to more negative potentials as the concentration of the ligand is increased thereby showing the complex formation (vide table 1). The reduction is quasi-reversible[8-10]. The values of $E^r_{1/2}$ at different concentrations of the ligand have been obtained (vide table 1) by Gellings' method[11]. The plot of $E^r_{1/2}$ vs log C_x is a straight line (Fig. 1) indicating the formation of a single complex. The value of the co-ordination number 'j' comes out to be 2 and thus the composition of the complex is $[Mn(citr.)_2]^{4-}$. The value of the stability constant (β) obtained by Lingane's method[12] comes out to be 5.2×10^5.

TABLE 1—Mn(II)-CITRATE SYSTEM, $\mu = 1.0$

[Pot. citrate] M	$-E_{1/2}$ V (S.C.E.)	$-E^r_{1/2}$ V (S.C.E.)	Slope V
0.000	1.515	1.510	0.0421
0.010	1.536	1.530	0.0431
0.020	1.568	1.562	0.0440
0.030	1.579	1.570	0.0450
0.040	1.590	1.580	0.0451
0.050	1.596	1.586	0.0462
0.060	1.599	1.592	0,0460
0.070	1.606	1.598	0.0452
0.080	1.612	1.605	0.0440

$j = 2$, $\beta = 5.20 \times 10^5$

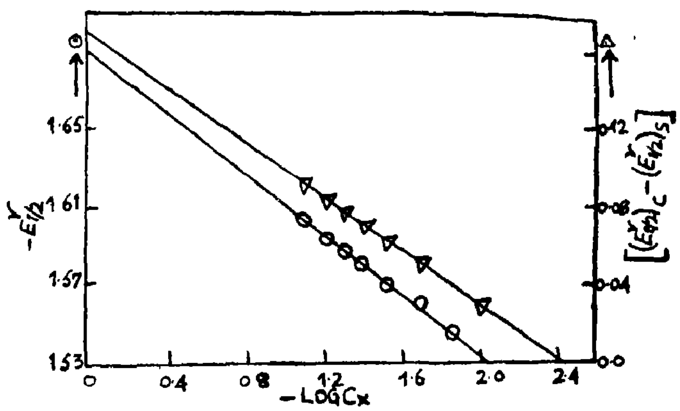


Fig. 1. Plots of $E^r_{1/2}$ vs. log C_x (—⊙—) and [$(E^r_{1/2})_c - (E^r_{1/2})_s$] vs. log C_x for Mn(II)-citrate system (—Δ—).

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Chalcones XXII : *Studies on Heterocyclic Chalcone Complexes of Copper(II) and Nickel(II)*

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THE use of aryl styryl heterocyclic ketones is almost unknown in the field of coordination chemistry. However, attempts have been made[1-5] to employ 2′-hydroxy chalcones as analytical reagents and to prepare complexes with some metal cations. Besides, the manifold biochemical activities[6-8] of quinolinyl chalcones and their coordinating nature with various cations is important. In the present communication, complexes have been isolated by treating 8-hydroxy-5-quinolinyl chalcone (HQC) with Cu(II) and Ni(II) in 90% (aq.) Methanol. The isolated complexes were characterised conductometrically, spectrophotometrically and by magnetic measurements.

All the reagents used were of A.R. and G.R. grade. Spectrophotometric studies were carried out using Bausch and Lomb spectronic-20. The ligand, 8-hydroxy-5-quinolinyl chalcone (HQC), was prepared as reported[6] and its homogeneity was checked by employing TLC[9]. The complexes were prepared by adding HQC solution (2 mole) to a hot aq. methanolic solution of metal chloride (1 mole). The resulting solution was refluxed for 3 hours, cooled, filtered and washed several times with cold alcohol to get the crystalline material. Bluish green Cu(II) complex and yellowish green Ni(II) complex was crystallised from dioxan.

Conductometric titrations gave the stoichiometric ratio of the ligand to metal as 2 : 1. Molar composition of the complex was determined further by the molar ratio method and confirmed by their molecular formula. Magnetic measurements were carried out at 30° using Gouy's method ; μ_{eff} values of Cu(II) and Ni(II) complexes were found to be 1.83 and 2.01 B.M., respectively. Infrared spectra of ligand and the metal complexes were recorded in nujol mull using Beckmann spectrophotometer. Bands at 480 and 495 Cm^{-1} (Cu(II) complex) and 523 and 465 Cm^{-1} (Ni(II) complex) are indicative of metal to nitrogen and metal to oxygen linkage. No such bands were observed in the HQC spectrum. Stretching frequency of the (-OH) and (C-N) linkage at 3250 and 1665 Cm^{-1}, respectively, in the free ligand were shifted to lower values in the spectra of Cu(II) and Ni(II) complexes (indicative of M-N and M-O bond formation) as observed by Poddar and Das[10].

Acknowledgement

Thanks are due to UGC for financial assistance, Dr. S. K. Sinha, Principal, F.G. College, Raebareli for providing facilities and Director, CDRI Lucknow, for analytical work.

TABLE 1—ANALYSIS, MAGNETIC DATA AND IR BANDS OF COMPLEXES

Complex (Molecular formula)	Colour	% Metal		% Nitrogen		μ_{eff}	M−O	M−N
		Found	Calc.	Found	Calc.	B. M.	Cm^{-1}	
$Cu(C_{18}H_{12}O_2N)_2$	Bluish green	10.51	10.38	4.19	4.57	1.83	495	480
$Ni(C_{18}H_{12}O_2N)_2$	Yellowish green	9.87	9.22	5.21	4.63	2.01	465	523

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Molecular Interaction of Some Nonpolar Liquids with Dimethylsulphoxide. Osmotic coefficient and activity of solvent (DMSO) in Solution*

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DEPRESSION in freezing point in solutions of some nonpolar nonelectrolyte solutes namely benzene, toluene, carbontetrachloride and cyclohexane have been determined at different concentrations. The osmotic coefficient and activity of the solvent was calculated from freezing point depression data. The activity of the solvent tends to unity at infinite dilution in all the cases indicating that all solutions approach the ideal behaviour at infinite dilution.

The osmotic coefficient in all systems are nearly unity even at higher concentrations. This shows the absence of self association of these organic liquids in DMSO; also these systems do not appear to show any deviations from Roult's law. It indicates an appreciable dipole-induced dipole interaction between solute and solvent molecules which causes the solute molecules to remain unassociated.

In our previous studies[1], the molecular interactions between DMSO and some polar liquid like methanol,

TABLE 1—APPARENT MOLECULAR WEIGHT OF SOLUTE AND OSMOTIC COEFFICIENT AND ACTIVITY OF SOLVENT IN SOLUTIONS

Solute and its normal mol. wt(Mo)	Molality 'm'	Depression in freezing point ΔT	Apparent molecular weight M	Osmotic coefficient (ϕ) of DMSO	Activity (a) of DMSO
Benzene M_0= 78.11	0.1863	0.74	78.26	0.993	0.986
	0.2635	1.00	81.92	0.948	0.981
	0.3215	1.23	81.21	0.956	0.976
	0.4231	1.59	82.82	0.939	0.969
	0.4670	1.77	82.02	0.948	0.966
	0.6041	2.24	82.83	0.927	0.957
Toluene M_0= 92.14	0.0386	0.15	94.84	0.986	0.997
	0.0774	0.31	92.00	1.006	0.994
	0.1687	0.67	92.79	0.991	0.982
	0.2139	0.85	92 74	0.992	0.983
	0.2856	1.14	92.32	1.000	0.978
	0.4533	1.82	91.79	1.004	0.965
Carbontetrachloride (M_0=153.82)	0.1742	0.68	156.83	0.976	0.987
	0.2689	1.05	156.78	0.976	0.979
	0.3521	1.73	124.59	1.228	0.967
	0.4344	1.73	153.72	0.996	9.967
	0.5279	2.15	150.32	0.019	0.958
	0.6546	2.70	148.43	1.031	0.949
Cyclohexane M_0=84.16	0.1003	0.40	84.39	1.000	0.992
	0.1901	0.75	85.17	0.986	0.986
	0.2819	1.10	86.32	0.975	0.979
	0·3047	1.20	85.39	0.983	0.977
	0.4552	1.82	84.19	1.000	0.956
	0.4722	1.89	84.09	1.001	0.964

* Presented at the convention of Chemists, 1976

ethanol, cyclohexanol, chlorobenzene and nitrobenzene have been worked out from cryoscopic measurements. All the polar liquids are found to be unassociated in DMSO showing a strong dipole-dipole interaction in solution. It seems therefore, very interesting to see how nonpolar liquids behave in DMSO because question of dipole-dipole interaction does not arise in case of nonpolar liquids. Some nonpolar liquids namely benzene, toluene, carbontetrachloride and cyclohexane are chosen for the present studies, and osmotic coefficient and the activity of solvent (DMSO) is determined in solutions of these liquids from cryoscopic measurements.

Experimental

DMSO (Fluka, purum grade) and all other liquids were used after purification in the manner described earlier[2].

The simple Beckman apparatus was used for measuring depression in freezing point ($\triangle T$) in solutions. The rest of the procedure for measuring depression in freezing point and calculating apparent molecular weight of solute and osmotic coefficient and activity of solvent was as given in our previous studies[1].

Results and Discussion

The values of apparent molecular weight of solute, osmotic coefficient 'ϕ' and activity 'a' of solvent (DMSO) in different systems at different concentrations are given in Table 1.

It may be noted from Table 1 that all the solutes have nearly normal molecular weights in DMSO. Since the solutions used are not very dilute, hence there is erratic change in the apparent molecular weight of the solutes.

Osmotic coefficients in all systems are nearly unity at higher concentrations. This shows the absence of self molecular association of these organic liquids in DMSO ; also these systems do not appear to show any deviations from Roult's law. It indicates an appreciable dipole-induced dipole interaction between solute and solvent molecules which causes the solute molecules to remain unassociated.

The activity of the solvent in different solutions decreases as the concentration of the solute in the solution increases. From the activity (a) data given in Table 1, 'a' vs m curves were drawn. Same type of straight line is observed in all cases. On extrapolating the straight lines to zero concentration, activity of solvent is found to be unity in every case, showing that solutions become more ideal in dilute range.

Acknowledgement

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Chemical Investigation on Some Mangrove Species Part IV. *Heritiera minor*, a typical Mangrove species

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IN continuation of our earlier report[1-3] on ecological influence on taxonomic variation, we report herein the chemical investigation of the leaves and barks of *Heritiera minor* (Fam. *Sterculiaceae*), a typical Mangrove species of Sundarban. It is a small tree with blend root sucker, The plant materials were collected in the month of December. No chemical work appears to have been reported on this genus.

Petroleum extract of the leaves was taken up in ether and separated into neutral and acidic fractions. The acidic fraction yielded waxy materials, yet to be characterised. The neutral part on column chromatography over silica gel G yielded the following fractions.

The first fraction furnished a solid material (0.25g), m.p. 245°, $C_{30}H_{50}O$ (M^{+}426). IR absorption at 1715 cm^{-1}, mass fragmentation pattern and NMR signals showed its identity with friedelin ; oxime, m.p. 286°.

Second fraction was triacontanol (0.07g), m.p. 82°.

Third fraction which registered intense spot with Rf 0.42 (solvent : chloroform) on repeated recrystallisations from benzene-alcohol yielded two crystalline materials, compounds A (0.70g) and B (3.50g). Compound A had m.p. 268°, $[\alpha]_D \pm 0°$, ν_{max}^{KBr} 3400 (–OH), 1635 and 812 cm^{-1} (double bond) ; M. S. m/e 426(M^{+}) ; acetate, m.p. 300°, and was identified as taraxerol. Compound B, m.p. 195°, isolated from the filtrate of compound A was purified through preparative tlc. Superimposable IR spectrum and co-glc on 3% SE-30 on gas chrome-Z, 60-80 mesh (Ret. time : 17.0 mins at 250° – 52°) showed its identity with β-amyrin.

The last fraction was β-sitosterol, m.p. 138°. The bark of *H. minor* on similar work-up showed the presence of all the constituents of leaves with lower yield in each case.

Acknowledgement

The authors are highly indebted to Dr. A. Ghosh of Bose Institute, Calcutta for glc studies.

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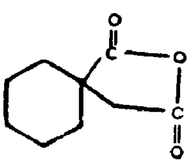
Methanolysis of the Anhydride of 1-Carboxycyclohexane-1-Acetic Acid : A Comment.

JAYANTA K. RAY*

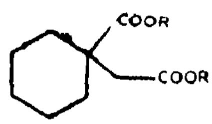
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In contradiction to the earlier reports by Khuda and Bhattacharya[1], who depicted the formation of the half-ester-acid (III) by methanolysis of the anhydride (I), Saharia and his co-workers[2] have recently reported that methanolysis of the anhydride (I) produces the isomeric half-ester-acid (II) as the only product.



(I)



(II) $R=CH_3$, $R'=H$
(III) $R=H$; $R'=CH_3$
(IV) $R=R'=C_2H_5$
(V) $R=C_2H_5$; $R=H$
(VI) $R=R'=CH_3$

In connection with synthetic studies in resin acids it was reported from this laboratory[3] that partial hydrolysis of the diethyl ester (IV) gives the mono acid ester (V). Accordingly, partial hydrolysis (5% methanolic potassium hydroxide—1 hr) of the dimethyl ester (VI), [n.m.r. δ (CCl_4) 1.51 (br s, 10H, methylene), 2.50 (br s, 2H methylene), 3.60 (s, 3H,-CH_2-$COOCH_3$) and 3.65 (s, 3H,-$COOCH_3$)] prepared from the corresponding diacid[4,5] by esterification with an excess of ethereal diazomethane, produces the half-acid ester (II) as the major acidic product, m.p. 56° [^1H n.m.r. δ(CCl_4) 1.50 (br s, 10H, methylene), 2.55 (br s, 2H, -CH_2-COOH), 3.65 (s, 3H, t-$COOCH_3$) and 10.00 (br s, 1H, COOH, exchangeable with D_2O)]. In the present study the methanolysis of anhydride (I) according to Saharia and his co-workers[2] afforded a mixture of two half-acid esters (II) and (III) containing *Ca* 10-15% of (II) as estimated from the integration ratio of the respective methyl ester singlets in the ^1H n.m.r. spectrum. After repeated column chromatography on silica gel using petroleum ether – ether (9:1), eluents furnished the pure half acid ester(III) [^1H n.m.r. δ(CCl_4) 1.50 (br s, 10H methylene), 2.53 (br s, 2H,-CH_2-$COOCH_3$), 3.60 (s, 3H, -$COOCH_3$) and 10.80 (s, 1H, >C–COOH, exchangeable with D_2O)] as a thick liquid. The present reinvestigation thus confirms again the general observations[6] recorded for the opening of substituted succinic anhydrides by treatment with alcohols.

The author thanks Prof. U. R. Ghatak for his suggestion to undertake this problem, which was brought to his notice by Dr. P. C. Bhattacharya, Department of Chemistry, Vidyasagar College, Calcutta.

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Chemical Investigation on *polyPodium juglandifolium* Don.

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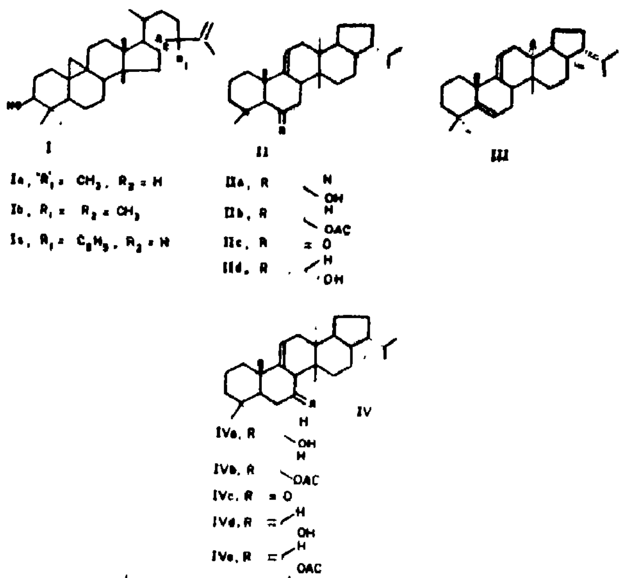
The neutral fraction of the benzene extract of the fern *Polypodium juglandifolium* Don on careful chromatography afforded two hydrocarbons together with six alcohols shown in Table 1.

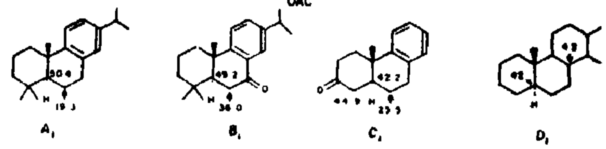
Fernene, filicene, cyclolaudenol and dryocrassol were identified by direct comparison with authentic specimens (m.m.p and Co-IR). The mother liquor from the crystallisation of cyclolaudenol was seen to be a mixture of two compounds one of which was cyclolaudenol (TLC). The mixture of alcohols (A), m.p. 121–22°, on acetylation gave an acetate (B), m.p. 107-108°, $(\alpha)_D$ + 55.17° and on catalytic hydrogenation in presence of Pd-C gave a compound (C), m.p. 132-34°, which on acetylation gave an acetate (D), m.p. 127-28°. NMR spectra of the original mixture (A) and its acetate (B)

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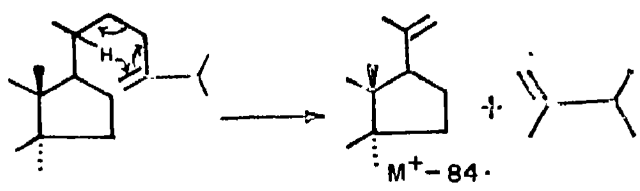
TABLE 1—PHYSICAL CONSTANTS OF COMPOUNDS ISOLATED FROM *P. Juglandifolium*

Sl. no.	Compound (Str. no)	M. p. (°C)	$[\alpha]_D$	Mol. formula
1.	Fernene[1]	169–70	−16.3°	$C_{30}H_{50}$
2.	Filicene[1]	231–32	+49.6°	$C_{30}H_{50}$
3.	Cyclolaudenol[1](Ia)	122–23	+45°	$C_{31}H_{52}O$
4.	Cycloneolitsol(Ib)	176–80	–	$C_{32}H_{54}O$
5.	Polypodinol A[2](IIa)	223–25	−89.13°	$C_{30}H_{50}O$
6.	Polypodinol B[3](IVa)	165–66	+28.57°	$C_{30}H_{50}O$
7.	Dryocrassol[4]	245–47	+65°	$C_{30}H_{52}O$
8.	Polypodinol C(IVd)	149–51	−3.28°	$C_{30}H_{50}O$





both showed distinct peaks at δ 4.65 ($-CH_2$) and 4.68 -(3H, $-CH_2$, -*CH* OAc) respectively but in the corresponding spectrum of (C) the peak due to vinylidene group was absent indicating that both the compounds in the mixture contained a $-CH_2$ group. Oxidation of the mixture (A) with Jones reagent gave a mixture of ketones (E), m.p. 117-18°. Mass spectra of (A), its acetate (B), the dihydro-compound (C) and its acetate (D) indicated that along with cyclolaudenol (M^+ 440) a second component (M^+ 454), that is, a new C-32 triterpene alcohol $C_{32}H_{54}O$ was present in the mixture (A). The mass spectral fragmentation shown in Table 2 when examined with the fragmentation pattern of cyclolaudenol Ia[5,6,7] clearly indicated that the new compound was closely related to cyclolaudenol having an extra carbon ($-CH_2$) in the side chain[1]. The position of the double bond ($-CH_2$, NMR) in the side chain may be tentatively assigned from the mass spectrum of (A) as the M-84 fragment observed in the McLafferty rearrangement involving the 24, 28 double bond[5,8] and the C(20) hydrogen has been found to be absent.



From the foregoing evidence, two probable structures Ib[9,10] and Ic can be assigned to the new C-32 compound. After extensive PLC of the mixture of alcohols (A) cyclolaudenol (Ia) and 5 mg of cycloneolitsol (Ib)[9-12], m.p. 176-80°, could be isolated. The acetate of the latter, m.p. 165-67°, was found to be identical with a sample of cycloneolitsol acetate.

TABLE 2—MASS SPECTRAL FRAGMENTS OF COMPOUNDS (*m/e* VALUES)

Compound	M	M−15	M−18 or M−HOAc	M−18−15 or M−HOAc−15	Other fragments				
(A)	440 454	425 439	422 436	407 421	300 314	379 393	175	315	
(B)	482 496	467 481	422 436	407 421	300 314	379 393	175	357	297
(C)	442 456	427 441	424 438	409 423	302 316	381 395	175	315	
(D)	484 498	469 483	424 438	409 423	302 316	381 395	175	357	297

Polypodinol A (Table 1) ν_{max}^{nujol} cm^{-1} 3605 (OH), gave the acetate IIb, m.p. 203-204°, $(\alpha)_D$-83.72°, ν_{max}^{nujol} cm^{-1} 1725, 1245 ; NMR ($CDCl_3$) of IIa δ 0.8-1.28 (8 t-CH_3). 5.40 (*m*., trisubstd. double bond) and 4.40 (-CH-OH) and IIb δ 0.8-1.18 (8 t-CH_3), 2.0 (3H, -O.CO.CH_3), 5.40 (*m*, 1H, vinyl proton), 5.20 (1H, *CH*-OAc) suggested it to be a secondary alcohol in a triterpenoid skeleton. IIa & IIb did not show any UV absorption in the region 200-300 nm. CrO_3-Py oxidation of IIa gave a ketone IIc $C_{30}H_{48}O$ (M^+424), m p. 221-23°, $(\alpha)_D$+16.06°, ν_{max}^{nujol} cm^{-1} 1720. Wolff-Kishner reduction of IIc gave fernene, m.p. 168-69°, $(\alpha)_D$-16.6° (identical with an authentic sample) indicating that IIa is a hydroxy derivative of fernene. MS of IIa *m/e* 426, 339, 271, 257 strongly suggested that (OH) group is present in ring A or B. C D. curve of the ketone IIc showed a strong positive Cotton effect $\Delta\epsilon$ 3.39 at 296 nm. Inspection of the Dreiding model suggest that the C-6 ketone would adopt a twist conformation with a positive Cotton effect but a C-7 ketone ($\beta\gamma$-unsaturated) would most probably give rise to a negative Cotton effect[18]. This is further confirmed by CMR Spectrometry. In the spectrum of fern-9 (11)-ene, a signal at 52.1 ppm is assigned to C-5 and that at 59.7 ppm to C-8 (estimated 50 and 55 ppm respectively by comparsion with model compounds $A_1 - D_1$). If 13 ppm is added for the effect of an α-carbonyl[14], the predicted values are in good agreement with the observed ones (Table 3).

TABLE 3 – CMR CHEMICAL SHIFTS OF IIc AND IVc

Compound	Predicted (with models A_1, B_1, C_1, D_1)	Predicted (with fernene as model)	Found
6-keto (IIc)	$CH(C_5)65$	65.1	63.4
	$CH(C_8)52$	59.7	54.5
	$CH_2(C_7)44$	—	42.6
7-keto (IVc)	$CH(C_8)67$	72.7	70.9
	$CH(C_5)49$	52.1	47.1
	$CH_2(C_6)36$	—	35.0

Dehydration of IIa with $POCl_3$-Py afforded a single product III (TLC), m.p. 157-58°, no UV absorption in the region 220-300 nm, NMR ($CDCl_3$) : δ 5.28 (m) and 5.44 (m) [two vinyl protons), indicating β-axial orientation of the (OH) group at C-6. $NaBH_4$ reduction of the ketone IIc gave the epimeric (6α-OH) compound IVd, m.p. 200-201°, acetate m.p. 177-79°. Oxidation gave back the original ketone.

Polypodinol B (Table 1) ν_{max}^{nujol} cm^{-1} 3590 (OH), NMR ($CDCl_3$) : δ 0.8-1.25 (8 t-CH_3), 5.40 (*m*, 1H, vinyl proton), 4.26 (-*CH*-OH), gave a monoacetate IVb, m.p. 207-208°, $(\alpha)_D$+38°, NMR ($CDCl_3$) : δ 0.8-1.16 (8 t-CH_3), 2.08 (3H, -O.CO.CH_3), 5.16 (*m*, CH_2-*CH*OAC). IVa showed no UV absorption between 220-300 nm. CrO_3-Py oxidation gave a ketone IVc, $C_{30}H_{48}O$ (M^+ 424), m.p. 174-75°, ν_{max}^{nujol} cm^{-1} 1720 (6-membered ring ketone), NMR ($CDCl_3$) : δ 0.8-1.04 8 t-CH_3), 5.38 (1H, vinyl proton). Wolff-Kishner reduction of IVc gave fernene identical with an authentic sample. IVc was different from 3-keto fern 9(11)-ene. C.D. curve of the ketone showed a strong negative Cotton effect. Examination of the Dreiding models with C-15 and C-16 ketone in the fernene nucleus separately suggests that the compound with C-15 ketone would have a very small Cotton effect probably positive, whereas the compound with C-16 carbonyl group would show a strong positive Cotton effect. Since a negative Cotton effect was observed, we believe that the carbonyl group is probably situated a C-7 as in IVc and polypodinol B is IVa. CMR of the ketone IVc (Table 3) also indicates the assigned structure.

Polypodinol C (Table 1) ν_{max}^{nujol} cm^{-1} 3430 (OH), NMR ($CDCl_3$) δ 0.8-1.2 (8 t-CH_3), 5.35 (1H, vinyl H), 4.4 (CH_2-*CH*-OH), gave a monoacetate IVe, $C_{32}H_{52}O_2$ (M^+ 468), m.p. 193-95° $(\alpha)_D$+30°, ν_{max}^{nujol} cm^{-1} 1720, 1245 (O.CO.CH_3), no UV absorption between 220-300 nm. CrO_3-Py oxidation of IVd gave a ketone, m.p. 168-70°, ν_{max}^{nujol} cm^{-1} 1725. Wolff-Kishner reduction of the ketone gave fernene indicating that IVd is a hydroxy derivative of fernene. C. D. spectrum of the ketone shows a strong negative Cotton effect for the carbonyl group, $\Delta\epsilon$-7.58 at 301 nm in methanol solution. The ketone m.p. 168-70° was found to be identical with 7-keto fernene IVc in all respects (m.m.p, IR, NMR, CMR), showing thereby that the polypodinol C was an epimer of polypodinol B. When IVc was reduced with sodium borohydride in methanol, it afforded an alcohol m.p. 151-52° identical with polypodinol C. Thus, polypodinol-C (IVd) is most probably the equatorial isomer and polypodinol B (IVa) is the axial isomer.

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Synthesis of New Schiff's Bases : Terephthalaldehyde Bis (Semicarbazone) and Terephthalaldehyde Bis (4-Phenylthiosemicarbazone)

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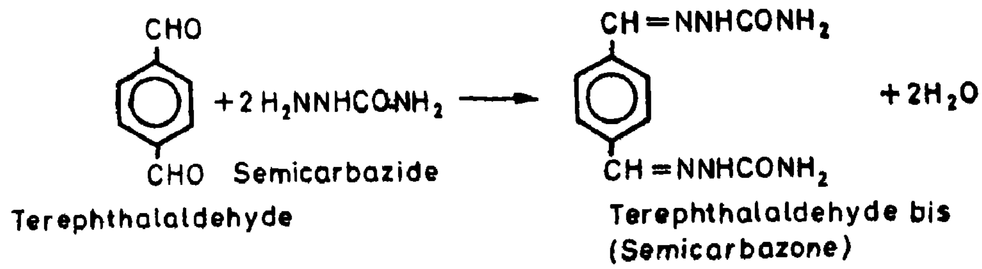
THE present communication is in continuation with the work[1–8] on coordination polymers in progress in these laboratories and describes the synthesis of bidentate coordinating ligands obtained by the condensation of terephthalaldehyde with semicarbazide or 4-phenylthiosemicarbazide. The reactions are :

The composition of compounds TPBS (I) and TPBPTS (II) have been established from elemental analyses data, and the structures elucidated through a study of infrared spectra (table 1).

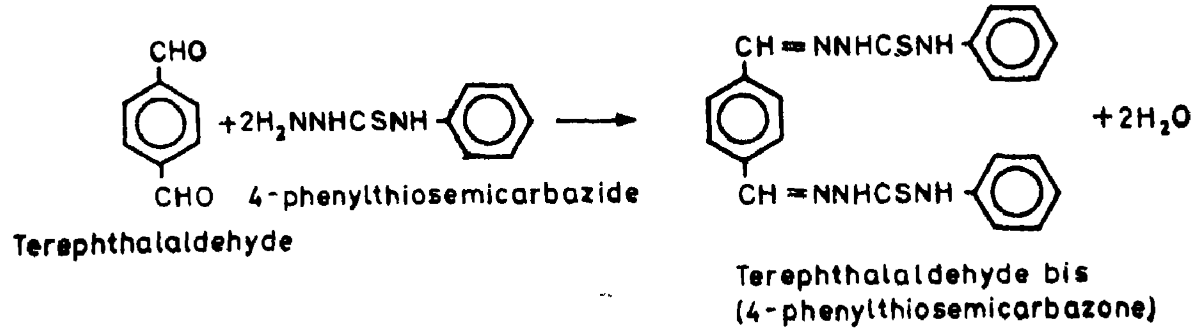
TABLE 1—INFRA-RED SPECTRA (CM^{-1}) OF TEREPHTHALALDEHYDE BIS (SEMICARBAZONE) AND TEREPHTHLALDEHYDE BIS (4-PHENYLTHIOSEMICARBAZONE)

TPBS	TPBPTS	Band assignments
3540s 3320m	3480m 3340w	N – H stretching
3020w 3000s	3040m	=C – H stretching
2320m	2330m	– C = N absorption of Schiff's base
1685s	1680vs	C = N stretching
1660s	...	C = O stretching
1645s 1640sh	1645s 1640sh	NH_2 deformation
1590vs 1540s 1500s	1590vs 1550s 1500s	C=C and C = N – N stretching vibrations
1495s 1440vs ...	1480s 1430s 1340vs	C = S and N – C – N stretching C – N stretching of the Ar-N type
1155s 1070vs	1140s 1080s	para-di substituted phenyl ring .
920vs 830s 730vs	975s 870s 750vs	C – H out of plane bending vibrations
495vs	450s	N – C – N deformation

s = strong, vs = very sharp, sh = shoulder, w = weak, m = medium



(I)



(II)

* For correspondence

The formation of Schiff's bases of 1:2 type (aldehyde: carbazide) is indicated from analysis. The presence of an aromatic type structure is recognised[4] by the presence of =C-H stretching vibrations near 3030 cm^{-1} and C=C vibrations in the region 1590 to 1500 cm^{-1}. The absorption bands observed near 3440 to 3340 cm^{-1} and 1645 cm^{-1} correspond to N-H stretching and NH_2 deformation, respectively. The strong absorption peak at 1660 cm^{-1} in the spectra of (I) is due to the presence of C=O group and C=S group in (II) is indicated by the peak at 1495 cm^{-1}. The C=N linkage of Schiff's base type[4] is confirmed by the bands near 2330 cm^{-1} in both the compounds. A very sharp absorption band at 1340cm^{-1} in the spectra of compound (II) shows the C-N stretching of Ar-N type. The C=N-N and N-C-N type linkages are shown by peaks near 1510 cm^{-1} and 1440 cm^{-1}[5].

The purity of the compounds were checked by TLC.

Experimental

Materials : Samples of terephthalaldehyde (Koch-Light) ; semicarbazide hydrochloride and 4-phenylthiosemicarbazide (Fluka), were employed. Solvents used were of reagent grade.

Preparation of terephthalaldehyde bis- (semicarbazone) (TPBS) : Semicarbazide hydrochloride, 11.15 g, 0.1 mole was dissolved in 100 ml hot water and 50 ml 1*N* NaOH solution was added. This solution was mixed with terephthalaldehyde (6.70 g, 0.05 mole dissolved in 100 ml ethanol) gradually with constant stirring. On shaking for a few minutes, a yellow coloured powdery solid separated. The whole mass was then refluxed over a waterbath for 1hr to ensure the completion of the reaction and the solid was filtered, washed with hot water, ethanol, and ether successively, and dried under reduced pressure over calcium chloride ; yield 86%. Found : C, 48.06 ; H, 4.53 ; N, 32.94 ; Calc. for $C_{10}H_{12}O_2N_6$; C, 48.32 ; H, 4.83 ; N, 33.57%.

The compound is insoluble in water, acetone, ethanol, chloroform, benzene, tetrahydrofuran, but has a little solubility in dimethylfomamide and dimethylsulphoxide.

Preparation of terephthalaldehyde bis-(4-phenyl thiosemicarbazone, (TPBPTS) : 8.35g, 0.05 mole 4-phenylthiosemicarbazide dissolved in 150ml ethanol was added to an ethanolic solution of terephthalaldehyde (3.35g. 0.025 mole dissolved in 50ml ethanol) and the mixture was refluxed over a waterbath for *ca* 2h. A yellow solid separated, which was left for few hours and filtered, washed with ethanol and ether, and dried under reduced pressure over calcium chloride ; yield 84%.

The compound is insoluble in water and other common organic solvents, but highly soluble in dimethylformamide and dimethylsulphoxide. Found : C, 60.67 ; H, 5.06 ; N, 19.50 ; Calc. for $C_{22}H_{20}N_6S_2$; C, 61.10 ; H, 4.66 ; N, 19.44%.

Infra-red absorption spectra : The i.r. absorption spectra were recorded with a Beckmann infra-red spectrophotometer in the range of 4000 to 400 cm^{-1} using KBr pellets.

Acknowledgement

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Unsaponifiable Matter of *Cordia rothii* Roem & Schult (Fruits)

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CORDIA rothii Roem & Schult[1,2,3] (N. O. Boraginaceae, Hindi-Gondi) has fruits of sweetish mucilagenous taste, aromatic agreable odour and good source of carbohydrates.

Due to its nutritive value it was taken up for phytochemical investigations. The present communication describes the study of the unsaponifiable matter from the fruits.

4 kg. powdered fruits on extraction with petroleum ether (40 – 60°) in a soxhlet extractor and removal of the solvent under reduced pressure yielded 75 g. of a yellow coloured fatty material. On saponification with 0.5 *N* KOH it yielded an unsaponifiable matter which was extracted with ether. Removal of ether gave a waxy residue (3.10 g.) which was subjected to column chromatography over 125 g. of alumina. The column was successively eluted with (i) petroleum ether (60 – 80°), (ii) petroleum ether (60 – 80°) : benzene (2:1) and (iii) benzene : chloroform (1:1). The three eluates were collected separately and solvent distilled off under reduced pressure. The residue from the eluates (i) on

crystallisation from acetone gave shining crystalline plates (m. p. 64°). The compound gave negative tests of all classes of compounds. Its stability, negative reactions with bromine water and $KMnO_4$ suggested its saturated nature. It was identified as n-hentriacontane by mixed m.p. and co-chromatography with authentic sample. IR and NMR data further confirm its identity as n-hentriacontane.

The residue from eluates (ii) on crystallisation from a mixture of chloroform and methanol (1:1) yielded white flakes m.p. 199°, $[\alpha]_D^{35}+87°(CHCl_3)$, its acetate, m.p, 237°, $[\alpha]_D^{35}+80°$ $(CHCl_3)$. It gave positive Liebermann-Burchard reaction and Nollers' reaction for triterpene. Mixed m.p. determination and co-chromatography with authentic sample confirmed it as β-amyrin.

The residue from eluates (iii) yielded another colourless compound, crystallising from methanol : ethylacetate (1:1), m.p. 136 – 7° ; $[\alpha]_D^{36}-31°.0$ $(CHCl_3)$. It gave positive Salkowski and Liebermann-Burchard reactions for sterol and was identified as β-sitosterol by mixed m p. and co-chromatography with authentic sample.

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Synthesis of Pyrazolyl Schiff Bases

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SCHIFF bases have gained prominence as pharmacologically important substances. They have anticancer or antituberculostatic activity[1]. Anticancer schiff bases[2] have been prepared by the condensation of aniline with substituted benzaldehydes. Pyrimidine schiff bases[3,4] were synthesised as possible anticancer agents. A careful literature survey revealed that no such schiff bases have been investigated in the pyrazolone series. In view of the marked pharmacological importance of this class of compound we thought it would be of interest to investigate the schiff bases having a pyrazolone nucleus. 1-Phenyl-3-methyl-2-pyrazolin-5-one on fusion with acetamide followed by alkaline hydrolysis and subsequent acidification yields the 1-Phenyl-3-methyl-4-acetyl-2-pyrazolin-5-one. Ethanolic solution of the methyl ketone when heated with aniline affords the schiff base. The formation of the schiff base has been confirmed by a single step synthesis involving the fusion of 1-Phenyl-3-methyl-2-pyrazolin-5-one with acetanilide at 200-20° for 6 hr. The identity of the two products obtained by the two different methods was established from the analytical values and mixed m.p. The I. R. absorption spectra of the two products were superimposable.

In the present communication 24 schiff bases were prepared using *o*-, *m*-, *p*- substituted aniline, benzidine, *m*-phenylene diamine, glycine, sulphadiazine and sulphaguanidine. In the case of *o*-nitro aniline no condensation product was obtained even though the reaction was carried out for 12 hr. in the presence of fused sodium acetate. Failure of the *o*-nitro aniline to undergo condensation is possibly due to the extremely weak basicity and steric hindrance. The formation of schiff bases have been proved from the following observations : (i) Failure to react with characteristic carbonyl reagents and therefore indicating that the ketonic group present in acetyl pyrazolone must have reacted with the amino groups of the compounds under reference, (ii) Positive test with ethanolic ferric chloride solution indicating the presence of a free $\geqslant C-OH$ group (keto-enol tautomeric form of $>C=O$ at position 5).

Experimental

1. *Synthesis of 1-Phenyl-3-methyl-4-acetyl-2-pyrazolin-5-one* : It was prepared as per our earlier method[5]. m. p. 58°, yield 60%.

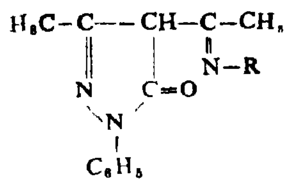
It was soluble in aq. sodium hydroxide and gave colouration with ethanolic ferric chloride solution.

2. *Synthesis of schiff base* : 1-Phenyl-3-methyl-4-acetyl-2-pyrazolin-5-one (0.01 mole and in the case of diamine 0.02 mole), aniline (0.01 mole), ethanol (20 ml) were heated on a water bath for 4 hr. On cooling the product that separated was filtered. Crystallisation from ethanol yields the shining pale yellow crystalline schiff base from aniline, m. p. 189°, yield 60% (Found : C, 74.11 ; H, 5.54 ; N, 41.21% $C_{18}H_{17}N_3O$ requires ; C, 74.22 ; H, 5.84 ; N, 14.43%).

Condensation with the substituted aniline, amino acid, diamine, benzthiazole sulphadiazine and sulphaguanidine were carried out exactly by the above procedure. The m. p. and analytical values are given in Table 1.

3. *Synthesis of schiff base (one step synthesis)* : An intimate mixture of finely powdered 1-Phenyl-3-methyl-2-pyrazolin-5-one (3 g.) and acetanilide (3 g.) was heated to 200-20° in an oil-bath for 6 hr. The dark coloured liquid was allowed to cool overnight. It was then treated with ethanol and allowed to stand for 96 hr. The solid thus obtained was filtered and washed with hot water to remove unaltered 1-Phenyl-3-methyl-2-pyrazolin-5-one and acetanilide and finally

TABLE 1—CONDENSATION PRODUCTS DERIVED FROM 1-PHENYL-3-METHYL-4-ACETYL-2-PYRAZOLIN-5-ONE



Sl. No.	Amino compounds used	Time of reflux in hrs	Formula of the product	m.p. °C	Yield %	Found % N	Found % S	Calcd. % N	Calcd. % S
1.	Aniline	4	$C_{18}H_{17}N_3O$	189	60	14.21	—	14.43	—
2.	*p*-Anisidine	4	$C_{19}H_{19}N_3O_2$	173	58	12.81	—	13.08	—
3.	*o*-Anisidine	4	$C_{19}H_{19}N_3O_2$	164	56	12.79	—	13.08	—
4.	*p*-Phenetidine	5	$C_{20}H_{21}N_3O_2$	198	55	12.31	—	12.53	—
5.	*p*-Toluidine	4	$C_{19}H_{19}N_3O$	168	60	13.54	—	13.77	—
6.	*m*-Toluidine	4	$C_{19}H_{19}N_3O$	153	57	13.51	—	13.77	—
7.	*o*-Toluidine	4	$C_{19}H_{19}N_3O$	161	54	13.49	—	13.77	—
8.	*p*-Chloroaniline	4	$C_{18}H_{16}N_3OCl$	177	56	12.63	—	12.92	—
9.	*m*-Chloroaniline	4	$C_{18}H_{16}N_3OCl$	172	53	12.66	—	12.92	—
10.	*o*-Chloroaniline	4	$C_{18}H_{16}N_3OCl$	157	52	12.69	—	12.92	—
11.	*p*-Bromoaniline	4	$C_{18}H_{16}N_3OBr$	187	57	11.12	—	11.35	—
12.	*p*-Nitroaniline	4	$C_{18}H_{16}N_4O_3$	197	53	16.41	—	16.66	—
13.	*m*-Nitroaniline	4	$C_{18}H_{16}N_4O_3$	184	51	16.37	—	16.66	—
14.	*p*-Amino Phenol	4	$C_{18}H_{17}N_3O_2$	274	54	13.71	—	13.68	—
15.	*p*-Aminobenzoic acid	5	$C_{19}H_{17}N_3O_3$	262	52	12.32	—	12.53	—
16.	Anthranilic acid	5	$C_{19}H_{17}N_3O_3$	216	52	12.35	—	12.53	—
17.	alpha-Naphthylamine	4	$C_{22}H_{19}N_3O$	167	60	12.24	—	12.31	—
18.	beta-Naphthylamine	4	$C_{22}H_{19}N_3O$	185	59	12.12	—	12.31	—
19.	Glycine	8	$C_{14}H_{15}N_3O_3$	250	42	15.49	—	15.38	—
20.	2-Aminobenzthiazole	6	$C_{19}H_{16}N_4OS$	186	47	15.84	8.95	16.09	9.19
21.	Benzidine	0.5	$C_{36}H_{32}N_6O_2$	242(d)	70	14.59	—	14.84	—
22.	*m*-Phenylenediamine	3	$C_{30}H_{28}N_6O_2$	232	63	16.37	—	16.66	—
23.	Sulphadiazine	8	$C_{22}H_{20}N_6O_3S$	240	40	18.51	6.92	18.75	7.14
24	Sulphaguanidine	3	$C_{19}H_{20}N_6O_3S$	278	60	20.12	7.48	20.38	7.76

purified from ethanol. m. p. 189°, Yield 30% (Found : C, 74.13 ; H, 5.56 ; N, 14.23% ; $C_{18}H_{17}N_3O$ requires ; C, 74.22 ; H, 5.84 ; N, 14.43%).

Acknowledgement

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Chemical and Pharmacological Investigation of *Pogestemon plactranthoides*

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THE chemical investigation of *Pogestemon plactranthoides*, revealed the presence of straight chain aliphatic hydrocarbon $C_{19}H_{40}$ and three sterols β-sitosterol, stigmasterol and campesterol. The pharmacological screening of the oil obtained from bracts, gave it's LD_{50} 550 mg/kg. The oil also exhibited significant potentiation of sleeping time induced by hexobarbitone, indicating a CNS depressant activity.

The plant *Pogestemon plactranthoides* belongs[1] to family Labiatae and reported to possess[2] enormous medicinal properties.

The preliminary pharmacological screening of the oil, obtained from pet. ether extract of the plant, gave LD_{50} value as 550 mg/kg i.p. The CNS depressant activity exhibited by the oil, was further substantiated by the significant potentiation of sleeping time induced by hexobarbitone.

A white low melting (m.p. 32°) aliphatic, straight chain hydrocarbon $C_{19}H_{40}$, was isolated from the oil. The identification of the hydrocarbon, was done with the help of combustion analysis and spectral data.

The chloroform extract of the plant furnished a colourless crystalline solid (m.p. 134-35°), which was identified to be β-sitosterol. The structure of β-sitosterol was ascertained by comparing the spectral data with that of authentic sample and preparation of derivative.

Though T.L.C. showed β-sitosterol to be homogenous in nature, mass spectrum revealed it to be a mixture of three compounds, with molecular peaks as 414, 412 and 400. The interpretation of the mass spectrum showed that along with β-sitosterol, other two compounds present were campesterol (M^+ 400) and stigmasterol (M^+ 412).

This is in agreement with the observations made by earlier workers[3,4] that whenever these sterols co-exist in nature it is extremely difficult to separate them to mass spectral purity.

Analysis of the ash of the plant showed the presence of iron and calcium. The presence of calcium salt may be quite significant in the light of antihaemorrhagic properties possessed[5] by calcium salt and the similar activity exhibited by the plant.

Acknowledgement

We thank Dr. T. R. Govindachari, Ex-Director, Ciba Research Centre, Goregaon, Bombay, for N.M.R. and Mass spectra. One of the authors (A.N.B.) is also grateful to U.G.C., New Delhi for the award of a J.R.F.

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Search for Possible Anti-Protozoal Compounds in the Quinoxaline Series

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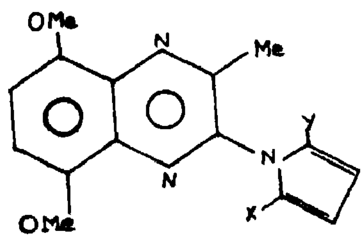
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QUINOXALINES having different substitutions are reported to possess wide range of antiprotozoal activity[1,2]. Investigation on the amebicidal activity of quinoxaline 1,4-(N,N')-dioxides and its substituted compounds[3], showed that the compounds were effective in acute amebic dysentry in man although none of them could be used due to toxic side effects. On the other hand many 1-substituted 4 or 5-imidazole derivatives are known to be active against *T. vaginalis*

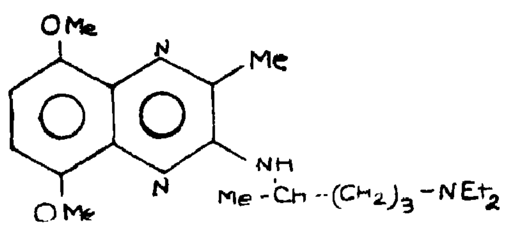
* To whom inquiries regarding this paper should be sent.

and *T. foetus*[4]. Metronidazole, the 1, 2, 5-trisubstituted imidazole derivative possesses high antiamebic as well as antitrichomonal activity[5]. Chloro quinoline is another highly active antiprotozoal compound which has a noveldiamine side chain in its structure[6].

Taking all these views under consideration quinoxaline derivatives of types (I) and (II) having nitro and/or methyl substituted imidazolyl and 4-diethylamino-1-methyl butylamino side chain have been synthesised to observe their antiprotozoal activity.



(I)



(II)

2-Hydroxy-3-methyl-5, 8-dimethoxy quinoxaline, prepared by the condensation of 1, 4-dimethoxy-2, 3-diaminobenzene[7,8] and pyruvic acid, has been chlorinated with $POCl_3$ to obtain the corresponding 2-chloro quinoxaline derivative which on interaction with the appropriate imidazole or novoldiamine has yielded the desired 2-substituted quinoxaline compounds (I and II).

Pharmacology : None of the compounds described in this paper were found to be significantly active *in vitro* against *E. histolytica*, *T. vaginalis* and *T. foetus* at a concentration of 12.5 mg/ml.

Experimental

2-Hydroxy-3-methyl-5, 8-dimethoxy quinoxaline :

An ice cold solution of pyruvic acid (4.4g), 1, 4-dimethoxy-2, 3-diamino benzene (8.4g) and dry benzene (25 ml.) was boiled in a 250 ml round bottomed flask provided with a Dean and Stark attachment in an oil bath at 120-130° until no more water collected. Finally benzene was distilled off and the residue left in the vessel was leached with aqueous $NaHCO_3$ (50 ml, 10%) to afford a solid (5.5g) which after washing with water was crystallised in yellow needles from aq. ethanol (yield 50%), m.p. 236-37° ; ir (nujol) 3400 (OH, NH), 1670 (amido carbonyl), 1435 ($\rangle C\text{-}CH_3$), 1648 (-C=C- , and -C=N-) cm^{-1} ; NMR ($CDCl_3$)δ 7.9 and 7.7 (1H each, d ; phenyl), 4 and 3.9 (3H each, S ; OMe), 2.65 (3H, S ; CH_3). (Found : C, 59.55 ; H, 5.15 ; N, 12.23. $C_{11}H_{12}O_3N_2$ requires C, 60.00 ; H, 5.45 ; N, 12.73%).

2-chloro-3-methyl-5, 8-dimethoxy quinoxaline :

2-Hydroxy - 3-methyl-5, 8-dimethoxy quinoxaline (5.5g) was refluxed with $POCl_3$ (28 ml) at 120-30° in an oil bath for 1 hr. Excess of $POCl_3$ was removed under reduced pressure. The residual mass was leached with water and was then extracted with a large volume of ether. On evaporation of ether a yellow solid (1.2g) was obtained. It was crystallised from ethanol in yellow needles ; yield 20% ; m.p. 174- 5°. (Found : C, 54.86 ; H, 4.29 ; N, 11.5. $C_{11}H_{11}N_2O_2Cl$ requires C, 55.34 ; H, 4.61 ; N, 11.74%).

The compounds (I & II) have been synthesised according to the method of Sen and Madan[2]. Method a : A mixture of 2-chloro-3-methyl-5, 8-dimethoxy quinoxaline (.01 mole), imidazole or its derivatives[9] or 4-diethylamino - 1-methyl - butylamine (.01 mole) and K_2CO_3 (.005 mole) was heated on a boiling water bath for 8 hrs., cooled and filtered. The residual mass left on evaporation was crystallised from a suitable solvent.

DATA ON 2-(1-IMIDAZOLYL)-3-METHYL-5,8-DIMETHOXY QUINOXALINE (I)

Formula	x	y	M.P. °C	Yield %	Analytical					
					Calcd %			Found %		
					C	H	N	C	H	N
(i) $C_{14}H_{14}O_2N_4$ (a)	H	H	112–14 (s)	80	62.22	5.18	20.74	62.31	4.92	20.29
(ii) $C_{14}H_{13}O_4N_5$ (a)	H	NO_2	107–8 (s)	75	53.33	4.12	22.22	52.9	4.32	21.9
(iii) $C_{15}H_{16}O_2N_4$ (a)	Me	H	106–7 (s)	70	63.39	5.63	19.71	63.3	5.23	19.25
(iv) $C_{15}H_{15}O_4N_5$ (a)	Me	NO_2	110–12 (s)	70	54.71	4.56	21.27	54.5	4.26	20.85

DATA ON 2-(4-DIETHYLAMINO-1-METHYL BUTYLAMINO)-3-METHYL-5,8-DIMETHOXY QUINOXALINE (II)

Formula	M.P. °C	Yield %	Analytical					
			Calcd %			Found %		
			C	H	N	C	H	N
(v) $C_{20}H_{32}O_2N_4$ (a)	115–16 (s)	70	66.66	8.88	15.5	66.16	8.39	15.25

a = method used for synthesis.
S = Benzene—Pet. ether (60–80°) mixture (1 : 1).

Acknowledgement

Authors thank M/S. Bristol Laboratories, Syracuse, N. Y., U. S. A., for antiprotozoal testing of our compounds.

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Synthesis of Potential Fungicidal Compounds

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4-THIAZOLIDINONES are well-known for their amoebicidal[1], hypnotic[2], anticonvulsant[3], mosquito-repellent[4] properties. It has also been shown to have a deep impact on antithyroid activity[5] with variation in the structure. The presence of N-C-S linkage in the compound has been shown to have antitubercular[6], antiradiation[7], nematocidal[8] and antifungal activity[9]. 2-Aryl-3-dialkylaminoalkyl-4-thiazolidinones were found to be much more active than procane which showed anaesthetic activity and some 2-aryl-3-alkylaminoalkyl-4-thiazolidinones have shown activity against sciatic nerve block in guinea pigs and spinal anaesthesia in rabbit[10]. 2-Aryl-3-alkyl-4-thiazolidinones were found to be active against psychomotor, anticonvulsant and barbiturate potentiating activity in mice[11]. Some of the 2-β-naphthylimino-4-thiazolidinones and their aryledene derivatives have been found to be fungicidal against *Alternaria palanduli*[12]. 2-Arylimino-3-aryl-4-thiazolidinones and their 1,1-dioxides were found to be effective against *Aspergillus niger*[13]. Bhargawa *et al.* have demonstrated that 2-arylimino-3-aryl-4-thiazolidinones possess considerable fungicidal activity[14-16]. Astik *et al.* synthesised 2-methyl-2-(2-hydroxy-5-methylphenyl)-3-aryl-4-thiazolidinones and showed that the introduction of -OH group increases the LD_{50} in mice[17]. In view of the significant biological applicability of 4-thiazolidinones, it was thought desirable to synthesise 2-methyl-2-(2-hydroxy-4, 5-dimethylphenyl)-3-substituted aryl-4-thiazolidinones in order to ascertain effect of substituent in the phenyl nucleus at 3-position of the 4-thiazolidinones on the fungicidal activity against *Helmynthosporium appatarnae*, not reported so far.

Experimental

General method of preparation of 2-methyl-2-(2-hydroxy-4, 5-dimethylphenyl)-3-aryl-4-thiazolidinone :

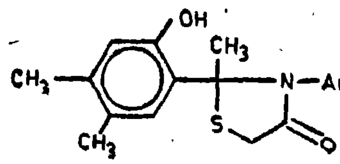
2-Hydroxy-4, 5-dimethyl acetophenone[18,19] (0.01*M*), aniline (0.01*M*) and thioglycolic acid (0.01*M*) were dissolved in benzene (100 ml) in a round bottomed flask and refluxed with a pinch of $ZnCl_2$ as a catalyst for 10 hr. Benzene was distilled off. The residue was washed with 2*N* HCl (10 ml) and then by 10% $NaHCO_3$ solution (50 ml), except in case of compound Nos. 18, 19, 20 in the Table, washed with water and recrystallised from 95% ethanol. The compounds prepared in 60-70% yield and their physical data are given in the Table.

All the I.R. spectra are taken in nujol mull and showed a sharp absorption peak at 3200-3300 cm^{-1} indicating the presence of free -OH group. A tertiary amide stretching frequency is also exhibited in the range of 1630-1660 cm^{-1}.

Antifungal screening

Antifungal screening of all 4-thiazolidinones was done by dry weight method. In general, the compounds were found to be inhibitory against *H. appatarnae* at 100 ppm. The parent compound and chloro, methyl, methoxy and nitro substituents in the *o*- and *p*- positions of the phenyl nucleus at 3-position showed relatively greater inhibitory effect as compared to the

TABLE



Sl. No.	Ar	Mol. formulae	M.P.* °C	Yield %	Nitrogen % Found	Nitrogen % Reqd.
1	Phenyl	$C_{18}H_{19}NO_2S$	77	70	4.77	4.47
2	*o*-Chlorophenyl	$C_{18}H_{18}ClNO_2S$	67	65	3.91	4.02
3	*m*-Chlorophenyl	do	95	62	4.00	4.02
4	*p*-Chlorophenyl	do	75	68	3.95	4.02
5	*o*-Methylphenyl	$C_{19}H_{21}NO_2S$	67	70	4.10	4.28
6	*m*-Methylphenyl	do	90	67	3.95	4.28
7	*p*-Methylphenyl	do	77	69	4.59	4.28
8	*o*-Methoxyphenyl	$C_{19}H_{21}NO_3S$	70	71	3.91	4.08
9	*m*-Methoxyphenyl	do	71	68	4.02	4.08
10	*p*-Methoxyphenyl	do	78	72	4.17	4.08
11	*o*-Nitrophenyl	$C_{18}H_{18}N_2O_4S$	62	63	7.71	7.82
12	*m*-Nitrophenyl	do	87	68	7.80	7.82
13	*p*-Nitrophenyl	do	110	66	7.70	7.82
14	*o*-Hydroxyphenyl	$C_{18}H_{19}NO_3S$	80	62	4.01	4.25
15	*m*-Hydroxyphenyl	do	65	63	3.80	4.25
16	*p*-Hydroxyphenyl	do	72	65	3.95	4.25
17	*p*-Bromophenyl	$C_{18}H_{18}BrNO_2S$	73	68	3.29	3.57
18	*o*-Carboxyphenyl	$C_{19}H_{19}NO_4S$	68	61	4.12	3.92
19	*m*-Carboxyphenyl	do	72	60	4.01	3.92
20	*p*-Carboxyphenyl	do	80	64	4.00	3.92

*Uncorrected

m-analogue, while compounds having *m*-hydroxy and *m*-carboxy groups were more inhibitory than the *o*- and *p*-isomers probably due to decrease in the acidity of the compounds because of the hydrogen bonding either with nitrogen or oxygen of the thiazolidinone.

Acknowledgement

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Book Review

Physics and Chemistry of Materials with Layered Structures, Volume I : Preparation and Crystal Growth of Materials with Layered Structures Pp. 280. Edited by, R. M. A. Lieth. Published by. D. Reidel Publishing Company, Dordrecht, Holland (Boston, U.S.A.), 1977.

THE present volume is the first in a series of 5 volumes covering the subject of "Physics and Chemistry of Materials with Layered Structures". The series has Dr. E. Mooser of the Laboratoire de Physique Applique as its Managing Editor. The present volume is edited by Dr. R. M. A. Lieth of the Technische Hogeschool, Eindhoven, who has himself contributed significantly to the field of materials with layered structure.

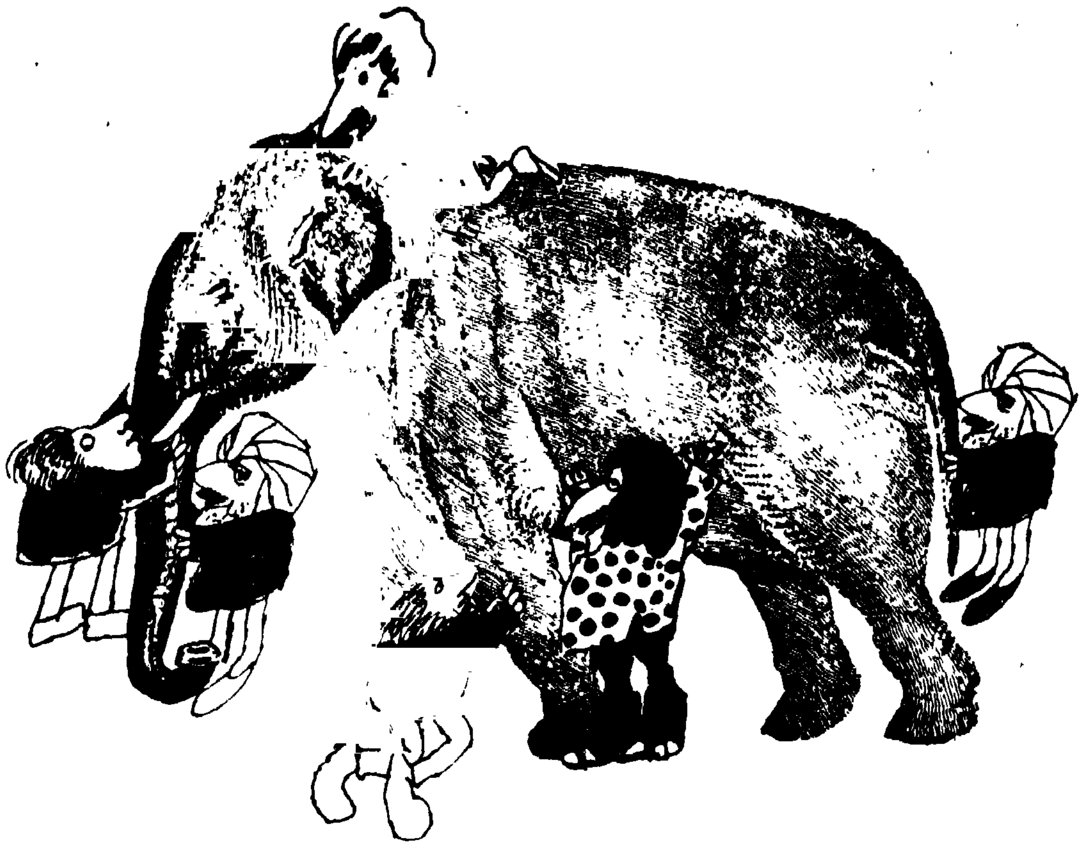
Graphite is the most well-known example of a material with a layered structure, and the book deals effectively with this material, but what the material scientist (chemist/physicist) is going to find most useful is large amount of data on the wide ranging materials—some of them quite unusual—which form layered structure. Since the prime purpose of this book is—as its title states—preparation and crystal growth, naturally this volume deals quite exhaustively with this aspect. Though the structural aspects are going to form the subject matter of subsequent volumes in this series, viz. volume 2 (Crystallography & Crystal Chemistry) and volume 5 (Structural Chemistry of Layer-type phases), this volume also deals with the structure and thermodynamic, properties of these compounds ; a knowledge and understanding of these properties is essential for devising newer methods of preparation and crystal growth. The volume is divided into six main topics, each written by a competent authority, and with a fairly complete bibliography upto 1974-75 ; some references of 1976 are also included : Elements (104 references) graphite, BN ; Metal Halides (245 ref.) ; Bivalent Metal Hydroxides (275 ref.) ; Transition metal dichalcogenides (137 ref.) 31 MCh_2 and their solid solutions ; III – VI compounds (75 ref.) and IV – VI compounds (102 ref).

The inorganic chemist, especially those engaged in the field of preparative inorganic chemistry will find the book very useful and it brings together in a fairly compact form, the various preparative techniques used to synthesize these compounds, especially in the form of single crystals. An important aspect of any preparation or synthesis, is a detailed characterization of the material especially with regard to its stoichiometry or the lack of it. The extensive bibliography quoted however reflects that material characterization is not being done as extensively as it ought to be.

The book however lacks uniformity of style, especially in respect of the use of SI units, which are used only in the first chapter. It is desirable that books published now should all use only the SI units. The reviewer wishes further that there was more critical and detailed evaluation of the different methods of preparation reported for a given compound, as it would have served as a useful guidepost to the neophyte. Nevertheless the volume makes a significant contribution and will provide a ready and convenient access to the methods of preparation for nearly all the known compounds with layered structure. Very interesting methods of preparation described are of relevance for the preparation of other compounds also, and hence the book deserves the attention of all inorganic chemists and material scientists.

The book is strongly recommended as a valuable contribution which, with its companion volumes, will provide the material scientists a cogent account of some very interesting and useful type of materials.

M. D. Karkhanavala.



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Oxalatofluorotitanates

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The preparation of $K_4[Ti_2O(C_2O_4)_3F_4].2.5H_2O$ and $[Co(NH_3)_6]_2[TiO(C_2O_4)F_2]_3.3H_2O$ are described. The compounds are studied through TGA, i.r. spectra and through X-ray analysis.

The conductometric and thermometric titrations of potassium titanyl oxalate by KF, AgF and by HF indicate the formation of the ion, $[TiO(C_2O_4)F_2]^{2-}$ in aqueous solution.

MANY oxalatotitanates are reported[1-6] in the literature but very little is known about oxalatofluorotitanates. Guerchais[7] reported (details unpublished) the presence of the species of the type, $[Ti_2F_8(C_2O_4)]^{2-}$ and $[TiF_4(C_2O_4)]^{2-}$. He studied the structural aspects of the above ions from ^{19}F NMR study in solution. In the present work, two new compounds, $K_4[Ti_2O(C_2O_4)_3F_4].2.5H_2O$ and $[Co(NH_3)_6]_2[TiO(C_2O_4)F_2]_3.3H_2O$ are reported. These compounds are studied through TGA, i.r. spectroscopy and X-ray analysis.

Moreover, the formation of oxalatofluorotitanate ions in solution was studied through conductometric and thermometric titrations of potassium titanyl oxalate by KF, HF and by AgF.

Experimental

The chemicals used in the present work were of reagent quality. Potassium titanyl oxalate, $K_2[TiO(C_2O_4)_2].2H_2O$ and hexamminecobalt(III) nitrate were prepared by standard methods[8,9]. Potassium was estimated as sulphate after prior separation of titanium. Titanium was estimated as TiO_2 through standard procedures. Cobalt was estimated by electrogravimetric method after separation of titanium as cupferronate. Fluorine was analysed gravimetrically as PbClF and nitrogen by semimicro Dumas' method. Oxalate was estimated permanganometrically in presence of boric acid (1-2 g).

Conductometric and thermometric titrations of potassium titanyl oxalate :

For each titration fresh solution was made by dissolving potassium titanyloxalate of known weight dissolved in known volume of carbon dioxide-free conductivity water. HF was standardised by titrating with caustic soda using phenolphthalein as indicator. For the preparation of standard KF solution, fluorine was estimated from it gravimetrically. Standard AgF was prepared by dissolving hydrated silver oxide in minimum volume of HF in such a manner that a little amount of silver oxide was left undissolved. The precipitate was filtered and silver and fluorine was estimated. Silver oxide was obtained as a precipitate from the reaction of $AgNO_3$ solution with caustic alkali. Excess of alkali was removed on washing with distilled water. The fluoride and HF solutions were preserved in polythene bottles. Calibrated polythene burette and pipette were used.

The conductance of the solutions were measured with a Phillips Conductivity Bridge No. PR 9500. A conductivity cell containing dip type platinum electrodes fitted in polythene stems was used. For each of the conductometric titration system consisting of potassium titanyl oxalate and fluorides/HF, three titrations were performed, viz., (a) a known volume (x ml) of standard potassium titanyl oxalate was titrated conductometrically by water (conductance values denoted as X), (b) a known volume (x ml) of water was titrated conductometrically (conductance values denoted as Y) by standard HF or KF or AgF and (c) a known volume (x ml) of potassium titanyl oxalate was titrated conductometrically (conductance of mixtures denoted as Z) by the same HF or KF or AgF that was used in the above titration. The difference of the conductance values $(X+Y-Z)$ was plotted against molar ratio $[HF \text{ or } MF]/[K_2TiO(C_2O_4)_2]$, where $M=K^+$ or Ag^+ and the results are reported in Figures 1, 2 and 3.

A thermometric titration of potassium titanyl oxalate by HF was carried out as before[10] and temperature change at constant volume (T_v) was plotted (Fig. 4) against the molar ratio $[HF]/[K_2TiO(C_2O_4)_2]$.

Preparation of oxalatofluorotitanates :

(1) *$K_4[Ti_2O(C_2O_4)_3F_4].2.5H_2O$:* Potassium titanyl oxalate (3.54 g) was dissolved in water (50 ml) and was mixed with potassium fluoride (1.16 g) also dissolved in water (10 ml). The *p*H of the mixture was lowered from 4.24 to 3.04 by adding 25 ml glacial acetic acid. The mixture was crystallised in a desiccator containing conc. H_2SO_4. The crystals were filtered, washed once with cold

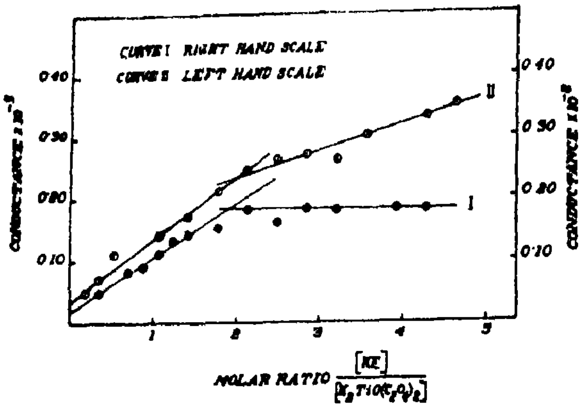


Fig. 1. Conductometric titration of potassium titanyl oxalate by KF at 30°.

Curve I. X represents the conductance recorded in the blank titration of 35 ml potassium titanyl oxalate (0.01 *M*) by water; Y represents the conductance recorded in the blank titration of 35 ml water by KF (0.25 *M*); Z denotes the conductance recorded in the titration of 35 ml potassium titanyl oxalate (0.01 *M*) by KF (0.25 *M*).

Curve II. X, Y and Z have the same significance as above in the titration of 35 ml potassium titanyl oxalate (0.001 *M*) by KF (0.025 *M*).

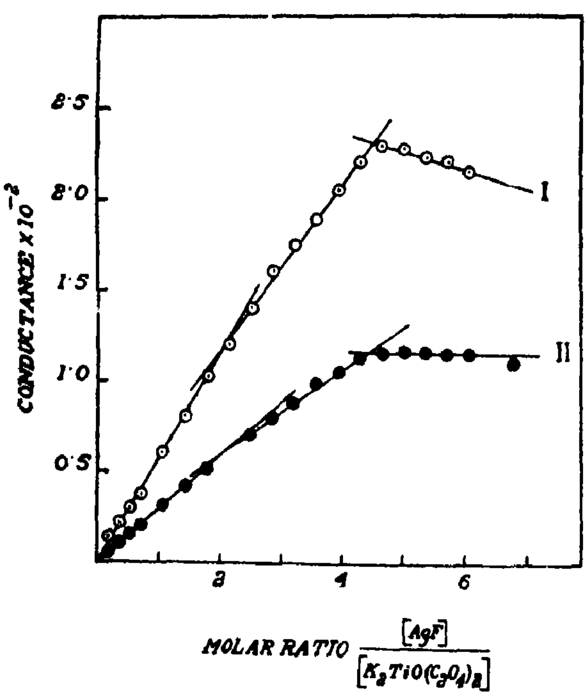


Fig. 2. Conductometric titration of potassium titanyl oxalate by AgF at 30°.

Curve I. X represents the conductance recorded in the blank titration of 35 ml potassium titanyl oxalate (0.01 *M*) by AgF (0.25 *M*); Y represents the conductance recorded in the blank titration of 35 ml water by AgF (0.25 *M*); Z denotes the conductance recorded in the titration of 35 ml potassium titanyl oxalate (0.01*M*) by AgF (0.25 *M*).

Curve II. X, Y and Z have the same significance as above in the titration of 35 ml potassium titanyl oxalate (0.005 *M*) by AgF (0.125 *M*).

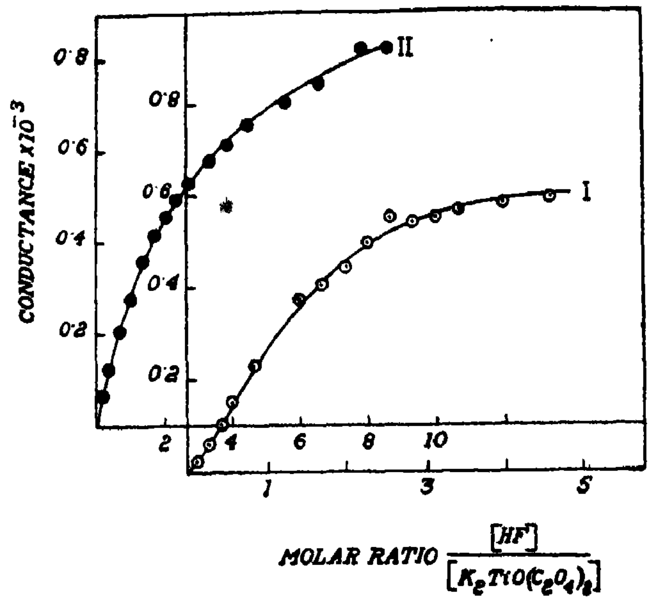


Fig. 3. Conductometric titration of potassium titanyl oxalate by HF at 30°.

Curve I. X represents the conductance recorded in the blank titration of 35 ml potassium titanyl oxalate (0.001 *M*) by water; Y denotes the conductance recorded in the blank titration of 35 ml water by HF (0.02 *M*); Z represents the conductance recorded in the titration of 35 ml potassium titanyl oxalate (0.001 *M*) by HF (0.02 *M*).

Curve II. Y and Z have the same significance as above in the titration of 75 ml potassium titanyl oxalate (0.001 *M*) by HF (0.10 *M*). X denotes the conductance of 75 ml potassium titanyl oxalate (0.001 *M*).

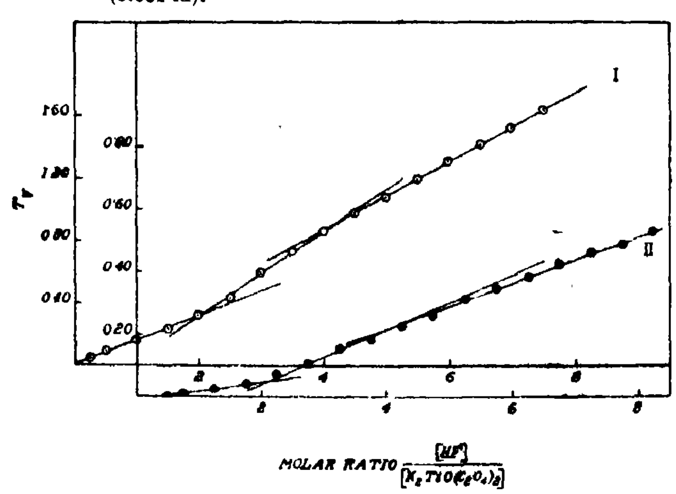


Fig. 4. Curve I. Thermometric titration of potassium titanyl oxalate (0.2 *M*) by HF (10 *M*).

Curve II. Thermometric titration of potassium titanyl oxalate (0.1 *M*) by HF (5 *M*).

water, pressed between the filter paper, and dried first in a desiccator containing KOH and then in air to constant weight.

Anal. Calcd: K, 23.94; Ti, 14.67; Oxalate, 40.42; F, 11.63%.

Found: K, 24.74; Ti, 14.46; Oxalate, 40.34; F, 11.89%.

(2) *$[Co(NH_3)_6]_2[TiO(C_2O_4)F_2]_3.3H_2O$*: Potassium titanyl oxalate (1.50 g) was dissolved in water (25 ml) and 12.75 ml. AgF (0.6643 M) was added with stirring in the ratio of $K_2[TiO(C_2O_4)_2]/AgF = 1/2$. The solution was filtered and to it hexamminecobalt(III) nitrate (0.88 g) dissolved in water (40 ml) was added, when precipitation took place immediately. The precipitate was filtered, washed once with cold water and then with rectified spirit. The compound was dried in air. The reaction can be represented as,

$$K_2[TiO(C_2O_4)_2]+2AgF = K_2[TiO(C_2O_4)F_2]+Ag_2C_2O_4.$$

$$3K_2[TiO(C_2O_4)F_2]+2[Co(NH_3)_6](NO_3)_3 = [Co(NH_3)_6]_2[TiO(C_2O_4)F_2]_3+6KNO_3.$$

Anal. Calcd.: Co, 12.46 ; N, 17.77 ; Ti, 15.20 ; Oxalate, 27.93 ; F, 12.06%.

Found Co, 12.35 : N, 17.21 ; Ti, 14.89 ; Oxalate, 28.00 ; F, 12.00%.

$K_4[Ti_2O(C_2O_4)_3F_4].2.5H_2O$ is white in colour. It could not be recrystallised from water. The hexamminecobalt(III) compound is light yellow and insoluble in water. Both the compounds are insoluble in common organic solvents. On drying over P_2O_5 in vacuum at room temperature both the compounds lose water molecules giving the corresponding anhydrous compounds.

Thermogravimetric studies: The data were recorded in a manually operated thermobalance. The heating rate for the compound, $K_4[Ti_2O(C_2O_4)_3F_4].2.5H_2O$ was 2°/minute and that of $[Co(NH_3)_6]_2[TiO(C_2O_4)F_2]_3.3H_2O$ was 5°/minute (Fig. 5).

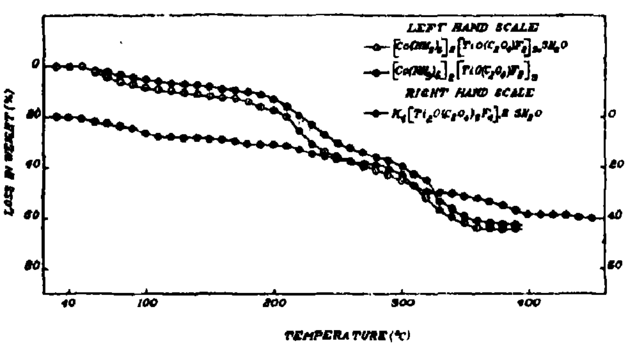


Fig. 5.

Infrared spectra: The data were recorded in a Perkin-Elmer apparatus in KBr pallets in the range 400-4000 cm^{-1} (Table 1).

X-ray studies: The X-ray powder diffraction data of $K_4[Ti_2O(C_2O_4)_3F_4].2.5H_2O$ were recorded in a G.E.C. diffractometer using Cu K_α radiations (Table 2).

TABLE—1 INFRARED SPECTRAL DATA

I	II	Probable band assignment (cm^{-1})
450-600(S, b)	500-600(S, b)	ν(Ti-F), ν(Ti-O), ν(C-C)
800(S)	715(vw) 800(S) 850(Sh) 900(Sh)	δ(O-C-O), ν(Ti-O)
1260(m) 1325(m)	1250(S)	ν_s(O-C-O) + δ(O-C-O)
1350(Sh)		δ(NH_3)
1400(S)	1400(S)	ν_s(O-C-O) + ν(C-C)
1685(S)	1690(S) 1725(S) } d 2920(vw)	ν_{as}(O-C-O), δ(NH_3), HOH
3100-3340(b) 3400-3600(w, b)	3450 3580 } d	νOH, ν(NH_3)

I. $[Co(NH_3)_6]_2[TiO(C_2O_4)F_2].3H_2O$
II. $K_4[Ti_2O(C_2O_4)_3F_4]_2.2.5H_2O$.
S = sharp, m = medium, w = weak, vw = very weak, b = broad, d = doublet and Sh = shoulder.

TABLE—2 X-RAY DIFFRACTION DATA

dA	Relative Intensity	dA	Relative Intensity
5.64	W	3.42	M
5.08	W	3.23	W
4.74	W	3.14	VW
3.86	VW	3.04	M
3.67	M	2.71	S
3.46	W	2.68	VS
		2.18	S

VS = Very sharp, S = Sharp, M = Medium, W = Weak, VW = Very weak.

Results and Discussion

The conductometric titrations of potassium titanyl oxalate by KF (Fig. 1) show breaks corresponding to the reaction ratio, $[TiO(C_2O_4)_2]^{2-}$: KF at 1 : 2 whereas conductometric titrations of potassium titanyl oxalate by AgF (Fig. 2) show breaks at 1 : 2 and 1 : 4 also. The probable general equation at the ratio, $[TiO(C_2O_4)_2]^{2-}$: MF (where $M = K^+$ or Ag^+) = 1 : 2 may be represented as:

$$[TiO(C_2O_4)_2]^{2-}+2F^- = [TiO(C_2O_4)F_2]^{2-}+C_2O_4^{2-}$$

The break at 1 : 4 in the conductometric titration of potassium titanyl oxalate by AgF is probably due to the reaction:

$$[TiO(C_2O_4)_2F_2]^{2-}+2AgF = [TiOF_4]^{2-}+Ag_2C_2O_4.$$

The above explanations are also supported from the thermometric titration of potassium titanyl oxalate by HF as shown below.

The thermometric titrations of potassium titanyl oxalate by HF (Fig. 4) show two breaks at the ratios 1 : 2 and 1 : 4. Besides, fine crystals of oxalic acid were found to be present in the reaction vessel at the end of the titration. The conductometric titration of potassium titanyl oxalate by HF (Fig. 3) also suggests the generation of stronger acid through the reaction. These reactions may be represented

as :

$$[TiO(C_2O_4)_2]^{2-} + 2HF = [TiO(C_2O_4)F_2]^{2-} + H_2C_2O_4.$$

$$[TiO(C_2O_4)F_2]^{2-} + 2HF = [TiOF_4]^{2-} + H_2C_2O_4.$$

The thermal decomposition study of potassium oxalate and sodium oxalate by different workers[11,12] suggested that these compounds become anhydrous by losing water of crystallisation at first and then formation of carbonates take place through the evolution of CO. But the pyrolysis curve of $K_4[Ti_2O(C_2O_4)_3F_4].2.5H_2O$ shows gradual loss in weight with rise in temperature. The curve does not show any horizontal stretch whatsoever, corresponding to the loss of water of crystallisation. The compound was found to be thermally stable up to 50°.

The thermogram of $[Co(NH_3)_6]_2[TiO(C_2O_4)F_2]_3.3H_2O$ indicates that the compound is stable up to 50°. The decomposition is quite rapid from 220° to 340°. The thermogram does not show any intermediate compound formation, not even the formation of anhydrous compound. The residue obtained at the constant weight (at 360°) was found to be the oxides of cobalt and titanium (loss in weight : Calcd : 66.09% $(Co_3O_4 + TiO_2)$; Found : 63.90%). The thermogram of anhydrous $[Co(NH_3)_6]_2[TiO(C_2O_4)F_2]_3$ does not show any remarkable difference from that of the hydrated one.

The infrared spectra of the compounds show that the oxalate groups present in the compounds are most probably acting as chelating ligands[13,14]. From the i.r. spectrum of $K_4[Ti_2O(C_2O_4)_3F_4]2H_2O$, it could not be ascertained whether any of the three oxalate groups is acting as a bridge between two titanium atoms.

The Ti-F bands occur in the region of 500-650 cm^{-1}[15-18]. Both the compounds show broad bands at 450-600 cm^{-1} which may be attributed to Ti-F stretching mode. But chelate oxalate compounds also show a band at 520-570 cm^{-1} which has been assigned to M–O and C–C stretching frequencies. Thus the superimposition of these bands on one another is not unlikely. Similarly superimposition of O–C–O deformation band on Ti–O band[19-22] is possible around 800 cm^{-1} which usually occur respectively at 800 cm^{-1} and 800-900 cm^{-1}. Besides, the i.r. spectra of $[Co(NH_3)_6]_2[TiO(C_2O_4)F_2]_3.3H_2O$ show typical frequencies of N–H at 3000-3400 cm^{-1}, 1550-1650 cm^{-1} and 1400-1470 cm^{-1}, etc.

The absorption in the region 3200-3550 cm^{-1} due to antisymmetric and symmetric OH stretching are observed in both the compounds, but the band at 1600-1630 cm^{-1} due to HOH bending[23] could not be identified probably due to the superimposition of the band with (O–C–O) asymmetric stretching.

The d-values of the compound, $K_4[Ti_2O(C_2O_4)_3F_4].2.5H_2O$ are compared with those of the compounds, $K_2C_2O_4.H_2O, K_2[TiO(C_2O_4)_2].2H_2O$ and KHC_2O_4[24] and it was found to be free from them.

The purity of the compound, $[Co(NH_3)_6]_2[TiO(C_2O_4)F_2]_3.3H_2O$ could not be ascertained from X-ray diffraction patterns due to the limited scope of the laboratory. In the case of this compound two things might happen; viz., (i) the reaction of potassium titanyl oxalate may take place in 1 : 4 ratio instead of 1 : 2 leaving behind half the total amount of potassium titanyl oxalate unreacted and the reaction of $[Co(NH_3)_6](NO_3)_3$ with unreacted half will give $[Co(NH_3)_6]_2[TiO(C_2O_4)_2]_3$ and (ii) there must be simultaneous formation of the compound $[Co(NH_3)_6]_2[TiOF_4]_3$. But it was seen that the conductometric titrations of potassium titanyl oxalate with AgF show distinct breaks at 1 : 2 and 1 : 4 ratio, probably indicating the stepwise removal of two oxalate ions. It was also seen that the reaction of the solution, obtained through the complete removal of oxalate ions by AgF in 1 : 4 ratio, with hexamminecobalt(III) chloride did not yield a pure compound of the type, $[Co(NH_3)_6]_2[TiOF_4]_3$. From these considerations it may be concluded that the compound, $[Co(NH_3)_6]_2[TiO(C_2O_4)F_2]_3.3H_2O$ is not a mixture of $[Co(NH_3)_6]_2[TiO(C_2O_4)_2]_3$ and $[Co(NH_3)_6]_2[TiOF_4]_3$ in 1 : 1 ratio.

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Complexes of Tin Tetrahalides with Some Aromatic Amine N-oxides

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Ten hitherto unknown complexes of SnX_4(X=Cl Br or I) with picoline N-oxide, quinoline N-oxide, isoquinoline N-oxide and 2, 2'-bipyridyl N, N'-dioxide have been synthesised and characterised through elemental analysis, molecular weight and conductance data. On the basis of IR spectral studies probable geometry for the complexes is proposed.

NUMEROUS coordination compounds of aromatic amine N-oxides with a wide variety of metal salts have been prepared and characterised[1]. There are also reports on adducts of some of these ligands such as pyridine N-oxide and 2,4-substituted pyridine N-oxides with tin tetrahalides[2-7]. In this communication we describe some hitherto unknown complexes of picoline N-oxide (PicO), quinoline N-oxide (QO), isoquinoline N-oxide (IsqO) and 2,2'-bipyridyl N,N'-dioxide ($BipyO_2$) with tin tetrahalides.

Experimental

Tin tetrachloride, -tetrabromide and -tetraiodide (BDH) were used without further purification. The Lewis bases employed were prepared by the reported methods[8-10].

The molecular adducts were prepared by the direct interaction of the Lewis acids and bases in absolute ethanol or absolute ethanol and diethyl ether using conventional ground glass apparatus. Manipulations were carried out in a dry box flushed with nitrogen.

The melting point of the complexes were determined on the electrically operated apparatus in open capillary tubes. The values reported being uncorrected. Most of the infrared spectra of the complexes were recorded in the range 4000-250 cm^{-1} using Perkin-Elmer 521 model at the Otto Mass Chemical Laboratories, McGill University, Montreal, Canada.

Crystalline adducts were isolated by one of the following methods.

(a) In a typical experiment 2.5 m. moles of tin tetrachloride in absolute ethanol (10 ml) was mixed with 5 m. moles of the Lewis base in the same solvent (20 ml) with continuous stirring. The precipitated solid was filtered, washed with ethanol, diethylether and dried in vacuum.

(b) 2.5 m.moles of tin tetrahalide in absolute ethanol (10 ml) was mixed with a solution of 5 m. moles of the ligand in the same solvent (20 ml) and the mixture was refluxed for 2-3 hrs. The excess solvent was distilled off and the residual viscous mass was treated with excess of diethylether to precipitate the desired complex. The product was washed and dried in vacuo. The experimental results are listed in Table 1.

Results and Discussion

The analytical data collected in Table 1 show that the adducts with $BipyO_2$ are of 1 : 1 stoichiometry whereas those with other amine N-oxides possess 1 : 2 molar ratio.

All the complexes possess high melting point and mostly decompose at their melting point. The chloride complexes are white whereas those of bromide and iodide possess pale yellow and orange colours respectively. They are non-hygroscopic except those of picoline N-oxide which are slightly moisture sensitive. The molecular weight of some of the complexes determined cryoscopically in nitromethane shows that they are monomeric in solution. Conductance measurements indicate absence of ionic species.

The absorption frequencies of diagnostic value namely NO stretching, NO bending and CH out-of-plane bending modes which are reported to be affected on complexation[1] are briefly discussed.

In the spectra of aromatic amine N-oxides examined an absorption of very strong intensity in the range 1265-1180 cm^{-1} has been assigned to NO stretching vibration mode. It undergoes a significant negative shift ($-\Delta\nu NO=20-87$ cm^{-1}) on complexation[1,11,12]. The decrease in the frequency is attributed to coordination from the oxygen atom of the base causing a decrease in π-character of the N–O bond. The extent of the negative shift of this mode of vibration has been employed to determine the relative donor ability of different amine N-oxides[14-16]. From the collected data the relative donor ability of various amine N-oxides examined towards tin tetrahalides may be expressed as follows :

$$\text{Pico} > \text{QO} > \text{BipyO}_2 > \text{IsqO}$$

TABLE—1 ANALYTICAL DATA AND IR ABSORPTION FREQUENCIES (CM^{-1}) FOR $SnX_4.nL$

X	nL	Method of Prep.	m.p.(°C)	%Analysis Found (calcd) Sn	C	H	N	Mol.Wt. (Found) (calcd)	ν_{NO}	δ_{NO}	γ_{CH}
–	PicO		–	–	–	–	–	–	1265vs	845s	773vs, 780vs
Cl	2PicO	a	206-8	24.40 (24.84)	30.49 (30.62)	3.21 (2.92)	4.50 (4.39)	452 (479)	1185vs 1170vs	810sh	800vs, 755vs
Br	2PicO	a	168-70	17.92 (18.11)	21.71 (21.91)	1.92 (2.13)	4.08 (4.26)	–	1180sh 1160vs	820m	800vs, 755vs
–	QO	–	–	–	–	–	–	–	1230vs	885s	795vs, 766s 725m
Cl	2QO	b	286-8(d)	20.92 (21.59)	38.92 (39.20)	2.32 (2.54)	5.25 (5.10)	495 (551)	1160s 1150s	880vs	805vs, 775s 735vs
Br	2QO	b	>300	15.92 (16.32)	29.91 (29.62)	2.11 (1.92)	3.98 (3.84)	–	1185s 1155s	882vs	815vs, 770s 730vs
–	IsqO	–	–	–	–	–	–	–	1182s	818s	740vs, 720vs
Cl	2IsqO	a	223-5	21.76 (21.59)	38.86 (39.21)	2.50 (2.54)	5.33 (5.10)	510 (551)	1155vs 1149vs	818s 806s	749vs, 732vs
Br	2IsqO	a	260-2	16.55 (16.32)	29.20 (29.62)	2.10 (1.92)	3.82 (3.81)	–	1151vs 1149sh	805vs	748vs, 731vs
I	2IsqO	a	130(d)	12.36 (12.90)	22.86 (23.55)	1.48 (1.55)	2.99 (3.05)	898 (917)	1150vs, br	805vs	749s, 725vs
–	$BipyO_2$	–	–	–	–	–	–	–	1264vs 1256vs	853s 841s	770vs, 728s
Cl	$BipyO_2$	a	336-8(d)	25.99 (26.50)	27.09 (26.72)	2.05 (1.78)	6.04 (6.23)	–	1207s 1192m	840s 825s	763vs, 722s 715s
Br	$BipyO_2$	a	328-30(d)	19.59 (18.97)	19.41 (19.13)	1.52 (1.27)	4.63 (4.46)	–	1202s 1190s	840s 825s	775vs, 725s 722s
I	$BipyO_2$	a	226-8(d)	15.02 (14.60)	15.12 (14.72)	0.99 (0.98)	3.54 (3.43)	–	1225vs 1215sh	848vs 833vs	772vs, 738s, 718s

The ν_{NO} vibration undergoes splitting on complexation which may be taken as an indication that the two ligand molecules occupy *cis* positions in the complexes possessing octahedral geometry.

An absorption of strong intensity in the range 900-800 cm^{-1} has been assigned to NO bending mode and from the tabulated data, it is apparent that only a slight shift of this vibration is observed on complexation[5,11,12], which may be attributed to two opposing effects, one similar to that of coordinated water where the bending vibration δOH is shifted towards higher frequency side and the other attributed to lowering in frequency caused by the decrease in π-character of the NO bond. As both the effects are almost equal and act in opposite direction, negligible shift in the absorption is observed.

Absorptions associated with C – H out-of-plane deformation modes are supposed to undergo slight positive shift due to tightening of the aromatic ring on complexation. A positive shift of ~20 cm^{-1} has been observed in this mode of vibration which is in conformity with the observations of earlier workers[5,11,12].

In the far IR region, there is a characteristic strong band in the range 400-300 cm^{-1} which is assigned to Sn – O stretching mode on the basis of reports on PyNO complexes of transition metals[11,12]. The displacement of the bond to higher frequency with increasing electronegativity of the halogen indicates a progressive increase in the Sn – O bond strength.

Tin-halogen stretching frequencies are sensitive to changes in the coordination number of the tin atom. Thus in tin tetrachloride the Sn – Cl stretching vibration appears at 403 cm^{-1} while it occurs at 332-308 cm^{-1} in all the chloro complexes reported here which is indicative of increase in coordination number of the tin atom.

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Mixed-ligand Complexes of Co(II), Cu(II) and Zn(II) with 1-Amino-2-Naphthol-4-Sulphonic Acid and Nitrogen Donor Ligands

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Nine mixed-ligand complexes of the type [ML_2B_2] where M = Co(II), Cu(II) and Zn(II). LH = 1-amino-2-naphthol-4-sulphonic acid and B is nitrogen donor ligand like quinoline, pyridine, gamma-picoline and diethylamine have been synthesised and characterised as octahedral complexes on the basis of analysis, conductance, magnetic susceptibility, IR and electronic spectral data.

IN our attempt to synthesise complexes of unusual coordination number, we have been trying for the base adduct formation of some divalent metal chelates. Several such base adducts of beta-diketonates and beta-ketoesters of Zn(II) and Cu(II) have been reported earlier[1-3]. It was therefore thought worthwhile to extend our investigation to the synthesis of some mixed-ligand complexes using 1-amino-2-naphthol-4-sulphonic acid as the chelating ligand.

Experimental

All the chemicals used were of AnalaR grade. Metal chelates were prepared by usual manner by reacting metal chlorides (Cobalt chloride 2.36 g, Copper chloride 1.69 g and zinc chloride 1.36 g) with ethanolic solution of 1-amino-2-naphthol-4-sulphonic acid (4.7 g) followed by the dropwise addition of ammonia. The compounds thus formed were suction filtered, washed with ethanol followed by ether and dried in vacuo.

Metal chelates were suspended in ethanol, mixed with the nitrogen donor ligands in 1 : 2 ratio and the mixture refluxed for about 1 hr., when a clear solution was obtained. On cooling the solution, crystalline compounds separated out. These were filtered, washed with ethanol, ether and dried in *vacuo*.

Metal contents in the complexes were estimated by complexometric E.D.T.A. method and nitrogen by standard micro analytical method. Conductance was measured in M/1000 DMF solution of the complexes using Toshniwal's conductivity bridge. IR spectra were recorded in KBr phase using Beckman IR-12 spectrophotometer. Electronic spectra were recorded using chloroform base solution of the complexes by Hilger-Watt UVSPECK spectrophotometer. Magnetic susceptibility measurements were carried out by Gouy method using Co[$Hg(SCN_4)$] as calibrant. Relevant analytical, conductance, magnetic susceptibility and IR spectral data are given in Table 1.

Results and Discussion

Complexes reported in the present investigation have the composition [ML_2B_2] where M = Co(II), Cu(II) and Zn(II) ; LH = 1-amino-2-naphthol-4-sulphonic acid and B is a nitrogen donor ligand like quinoline, pyridine, gamma-picoline and diethylamine, Cobalt(II) complexes are brown, copper(II) complexes are green and zinc(II) complexes are white in colour. All the nine complexes have fairly low melting points and low conductance values in DMF indicating non-electrolytic nature. Magnetic moment values show the presence of three and one unpaired electron in case of cobalt and copper complexes respectively and indicate a spin-free octahedral configuration for the cobalt and copper compounds.

The IR spectra of metal chelates and the corresponding base adducts are informative. Here 1-amino-2-naphthol-4-sulphonic acid can function as a bidentate chelating ligand using the hydroxyl oxygen and the primary amino nitrogen atom as the bonding sites, the sulphonic acid group remaining free probably due to steric reasons and spatial position. The C – O stretching vibrations in alcohols usually occur[5] in 1260-1000 cm^{-1} region which has appeared in the ligand at 1220 cm^{-1} and shifted to ~1200 cm^{-1} in the metal chelates indicating bonding of the oxygen atom. In the base-adducts, this band again shifts to higher frequency regions appearing at 1210 cm^{-1} indicating the bonding of the oxygen atom to the metal ion ν(N – H) in the chelating ligand appears at 3250 cm^{-1} as a sharp peak. In the metal chelates and base-adducts N – H stretching frequency appears either as a broad band or is split into several peaks not so sharp as in the parent compound proving indirect evidence for

TABLE—1 ANALYSIS, CONDUCTANCE, MAGNETIC SUSCEPTIBITITY, IR SPECTRAL DATA

Compound	M.P. (°C)	% Metal Found	% Metal Calc.	% N Found	% N Calc.	μ_{eff} B.M.	Ambos cm²	ν(C−O)	ν(N−H)	ν(M−O)	ν(M−N)
$[CoL_2(\gamma\text{-Pic})_2]$	210d	10.53	10.515	9.76	9.98	4.90	8.0	1210	3250	425	515
$[CoL_2Py_2]$	192	11.21	11.29	10.48	10.54	5.0	8.5	1210	3280	430	515
$[CoL_2(DEA)_2]$	205	11.27	11.88	10.51	10.78	4.95	10.0	1210	3260	420	510
$[CuL_2Q_2]$	187	9.88	10.30	8.74	8.80	1.82	9.8	1210	3250	440	510
$[CuL_2Py_2]$	173	11.85	11.90	10.26	10.45	1.80	8.8	1210	3250	430	505
$[CuL_2(\gamma\text{-Pic})_2]$	192	11.15	11.27	9.86	9.98	1.75	10.5	1210	3250	430	500
$[ZnL_2Q_2]$	169d	10.34	10.20	8.65	8.29	–	7.5	1210	3260	425	510
$[ZnL_2Py_2]$	202	12.07	12.09	9.47	9.85	–	10.2	1210	3250	420	510
$[ZnL_2(DEA)_2]$	189d	12.56	12.63	10.32	10.65	–	8.7	1210	3245	430	505

Q=quinoline, Py=pyridine, DEA=diethylamine, γ-Pic.=γ-picoline, d=decomposition

bonding at the nitrogen of the primary amino group. Most of the absorption bands due to free nitrogen ligands have been modified in the complexes proving indirect evidence of their presence as coordinated ligands. This has been further substituted[6] by the observation of ν(M−O) and ν(M−N) around ~430 cm^{-1} and ~510 cm^{-1} respectively which provide the direct evidence for the formation of metal chelates and their base adducts.

The cobalt(II) complexes in DMF solution give rise to two absorption bands with maxima at 8.6 and 19.7 K.K. region which can be assigned to $^4T_{1g} \rightarrow {}^4T_{2g}$ and $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transitions. These absorption bands, extinction coefficients and μ_{eff} values indicate a high-spin octahedral configuration. The copper(II) complexes show one broad absorption band centered at 15.0 K.K. Though three transitions $^2B_1 \rightarrow {}^2A_1(\nu_1)$, $^2B_1 \rightarrow {}^2B_2(\nu_2)$ and $^2B_1 \rightarrow {}^2E(\nu_3)$ occur in Cu(II) complexes of D_{4h} symmetry due to Jahn-Teller distortions, they are often very close in energy and give rise to a single broad band envelop.

Zinc(II) complexes have presumably an octahedral configuration on the basis of their analysis, conductance and IR spectral data.

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Studies on Chelation of Humic Acid with Some Polyvalent Metal Ions

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Investigations were made on interaction between certain bi, tri, tetra and hexa valent metallic cations with humic acid fraction isolated from alluvial soil of West Bengal by electrometric titrations and magnetic measurements. Electrometric titrations showed the formation of more than one chelates in each case and magnetic studies threw some light on the nature of the same.

THE stable complex formation of naturally occurring polyelectrolytes in soil, i.e. humic and fulvic acids with lower valent metal cations has been demonstrated by several workers[1,2]. These weakly acidic polyelectrolytes play a prominent role in the binding of micronutrients in soil and in determining the fate of toxic heavy metal pollutants in the environment[3]. It is now believed that ion exchange, surface adsorption, chelation, coagulation and peptization processes are involved in such interactions[4,5,6]. In the present paper attempt has been made to find out the nature of interactions of humic acid (HA) with some polyvalent cations, e.g., V^{+4}, Ti^{+4}, Mo^{+6}, Fe^{+2}, Cu^{+2} and Al^{+3}.

Experimental

Humic acid (HA) used in the investigation has been extracted and fractionated from Bigra Pond sediment (Burdwan), West Bengal by the standard method as stated earlier[7]. The HA fraction has been subjected to repeated resin (IR-120) treatment to decrease the ash content to the minimum (0.01%) in order to get sure that the ligand is free from metal ions.

For conductometric and potentiometric titrations the procedure as discussed in earlier paper[8] has been followed. The magnetic moments have been calculated from magnetic susceptibility measurement according to standard procedure[9].

Results and Discussion

The average molecular weight of HA as measured by electrometric method[10] has been found to be 2000. In the present discussion, the results are expressed on this basis.

Conductometric titrations

Instantaneous conductometric titration curves (Curves not shown here) are continuous in nature indicating no complex formation. But on allowing the reaction mixture to equilibriate for 24 hours, two breaks are noticed in each case of $HA-V^{+4}$, $HA-Ti^{+4}$, $HA-Mo^{+6}$ and $HA-Fe^{+2}$ combinations and one in each case of $HA\text{-}Cu^{+2}$ and $HA\text{-}Al^{+3}$ combinations. The molal compositions corresponding to these inflexion points are 1 : 6 and 1 : 8 for HA : Fe^{+2}, 1 : 3 and 1 : 5 for HA : V^{+4}, 1 : 2 and 1 : 4 for Ti^{+4}, 1 : 3 and 1 : 6 for HA : Mo^{+6}, 1 : 8 for HA : Cu^{+2} and 1 : 1 for HA : Al^{+3}.

During the titration of HA with Fe^{+2}, Cu^{+2}, Mo^{+6}, V^{+4}, Ti^{+4} and Al^{+3} cations conductances of the solutions increase after the formation of complexes. This is due to the fact that on interaction with metal cations highly conducting ionic species are resulted due to complex formation. Not only a strong electrolyte is produced from a weak electrolyte, but one of the ions formed is highly mobile, e.g., H^+. The sharp rise in conductance after the formation of the complex is thus due to the liberation of such mobile hydrogen ions to form hydroxylated metal-HA complexes. During the titration with NaOH solution the initial conductance of different metal-HA combinations are greater than HA alone. It may possibly be due to weak acidic nature of HA having very low degree of ionisation. On interaction with metal ions the conductances increase considerably due to formation of strong electrolyte and subsequent liberation of hydrogen ions.

Furthermore, the conductance difference between the curves increases as the solution becomes more alkaline indicating that the complexes are more stable in basic media. The fact that titration with NaOH resulting in a low conductance when the chelate is formed may be visualised from the following reactions—

$$HA + NaOH \rightarrow H_2O + Na^+ + A^-$$

$$nHA + M^{+n} + n\,NaOH \rightarrow n\,H_2O + n\,Na^+ + MA_n$$

The large MA_n would be expected to have a lower conductance than the smaller anion A^- since the

latter is extensively hydrolysed in an aqueous solution to give the highly conducting ions.

Potentiometric titrations

Titration curves (not shown here) of organic ligand in presence of metal salts show considerable drop in *p*H. Although some lowering in *p*H may be expected due to acidifying effects of the salts; experiments carried out in absence of humic acid showed that for the concentration of salts used such a drop in *p*H cannot be accounted for. One possibility is that H^{+} ions are released from an otherwise non-titrable functional groups of HA (e.g., phenolic OH)[14]. Such a drop in *p*H by the addition of metal salts of HA solution varies markedly with the metal ions. Martell and Calvin[11] point out that greater the tendency of metals to combine with a given chelating agent greater is the *p*H drop. From the present study it is noted that complexing tendency of the metal ions with HA follows the order

$$Mo^{+6} > V^{+4} > Ti^{+4} > Al^{+3} > Fe^{+3} > Cu^{+2}.$$

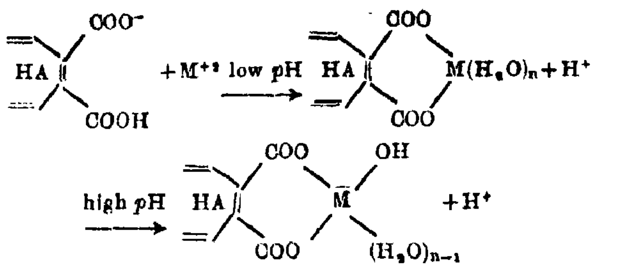
From titration curves of HA with NaOH no second ionisation of weaker acidic groups has been noticed but in presence of different metal ions such ionisations are prominent. It is evident that the weaker acidic groups like phenolic hydroxyls take part in reaction with metal ions producing free hydrogen ions. As more and more such groups interact with metal ions, possibility of HA-metal complexes increases[12] followed by marked *p*H change. As according to Wood[12] et al, some of the COOH groups HA occupy adjacent sites on aromatic rings, it is logical to assume that the mode of metal-HA interaction may be of the phthalic aoid type.

In order to get an idea about the mechanism of metal-HA interactions, the number of protons released by NaOH during the titration of HA and HA-metal mixtures are assessed in Tables 1(a) and 1(b).

TABLE—1(a)

*p*H	Number of protons released from HA/mole of base added
6.5	–
7.0	1.3
7.5	2.1
8.0	2.6
8.5	3.5
9.0	5.2

The general reaction leading to the release of protons may be represented as follows :



From Table 1(a) it is evident that at *p*H 7.0 approximately one COOH group has been titrated, similarly at *p*H 7.5, two, at *p*H 8.0, approximately three and at *p*H 9.0 two phenolic hydroxyl groups have been titrated in addition to the three COOH groups.

Data in Table 1(b) indicate that the number of protons released per mole of metal added is approximately one in all the cases up to *p*H 7.5. With further increase in *p*H there is gradual release of proton leading to the maximum value of two approximately at *p*H 9.0. Thus from the observed proton release data and the theoretical reaction it may be said that possibility exists for the formation of chelate type complexes between HA and polyvalent metal cations. This also corroborates the views of Schmitzer[18].

Magnetic properties

The magnetic moment data of different metal-HA complexes are given in Table 2.

TABLE—2

MAGNETIC MOMENTS FOR VARIOUS METAL-HA COMPLEXES (IN BOHR MAGNETONS) AT 27°

Complexes	Observed moments
V^{+4} – HA	1.8
Cu^{+2} – HA	2.0
Fe^{+3} – HA	5.4
Ti^{+4} – HA	1.7
Mo^{+6} – HA	1.75
Al^{+3} – HA	2.3

From the magnetic moments obtained above and on comparison of the same with standard values for these metal ions as such it may be said that the

TABLE—1(b) NUMBER OF PROTONS RELEASED FROM HA/MOLE OF METAL ADDED

*p*H	HA : Fe^{+3} (1 : 6)	HA : Fe^{+3} (1 : 8)	HA : V^{+4} (1 : 3)	HA : V^{+4} (1 : 5)	HA : Ti^{+4} (1 : 2)	HA : Ti^{+4} (1 : 4)	HA : Mo^{+6} (1 : 3)	HA : Mo^{+6} (1 : 6)	HA : Cu^{+2} (1 : 8)	HA : Al^{+3} (1 : 1)
6.0	0.3	0.4	0.8	1.1	0.5	0.4	0.7	0.8	0.9	0.6
6.5	0.5	0.5	1.2	1.2	0.7	0.8	1.2	1.2	1.0	0.9
7.0	1.1	0.9	1.4	1.4	1.1	0.9	1.2	1.3	1.1	1.05
7.5	–	–	1.5	1.6	1.3	1.2	1.5	1.4	1.2	1.2
8.0	–	–	1.6	1.7	–	–	1.6	1.7	1.4	1.3
8.5	–	–	1.8	1.8	–	–	1.7	1.7	1.5	1.4
9.0	–	–	–	–	–	–	1.9	1.9	–	–

observed values are slightly higher. This may be explained as due to the fact that the electric fields of the molecules surrounding the metal ions in its compounds restrict the orbital motion of the electrons and hence the orbital moments are partially quenched. The values of magnetic moments obtained in cases of V^{+4}, Cu^{+2}, Ti^{+4}, Mo^{+6} and Al^{+3} complexes indicate the presence of just one unpaired electrons. The high value of magnetic moment in case of Fe^{+2} complex can be accounted for low lying d levels of tetrahedrally coordinated Fe^{+2} ion when there is only a small second order orbital contribution to the magnetic moment[9]. Moreover, from the positive values of magnetic susceptibility data in case of Mo^{+6}, V^{+4}, Ti^{+4}, Fe^{+2} and Al^{+3} complexes it may be inferred that the metal ions are paramagnetic in the chelates. In case of Cu^{+2} complex however the susceptibility data is negative indicating diamagnetic nature of the metal ion in the chelate. One possibility for this is that the pairs of Cu^{+2} ions are held close together usually by carboxylate ions as a result of which the spins of the two Cu^{+2} ions are so strongly coupled that the dimer is diamagnetic.

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Ternary Complexes : Equilibrium Studies of Mixed-Ligand Complexes of Nickel Ion with Some Carboxylic and Phenolic Acids**

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The mixed-ligand chelates of nickel ion with aspartic, glutamic thiodiglycolic, thiodipropionic, malonic, malic, 5-hydroxysalicylic and 3, 5-dinitro salicylic acids have been investigated at 30° and μ=0.1M(NaClO$_4$) by pH metric method. Ni^{+2} forms 1 : 1 and 1 : 2 chelates with aspartic and glutamic acids and only 1 : 1 chelates with the remaining chelating agents, the mixed-ligand chelates being formed in a simultaneous and stepwise equilibria. Negative $\Delta \log K$ values for all the systems except glutamic-thiodiglycolic, malic-thiodipropionic, malic-thiodiglycolic and malic-3, 5-dinitro salicylic acids are ascribed to their differences in ring sizes. Intermediate $\Delta \log K$ values are expected when one of the ligand is carboxylic and the other phenolic acid.

A perusal of literature[1-4] shows that Ni^{+2} forms binary and ternary complexes with carboxylic and phenolic acids and Ni^{+2} complexes of thiocompounds have been reported biologically active[5]. A review of Sigel[6] clearly brings out biological importance and applications of simple and mixed complexes of Ni^{+2} with some selected ligands.

The present work is a continuation of our earlier work[7] and was undertaken with a view to find out whether Ni^{+2} forms complexes with the ligands chosen in a simultaneous or stepwise equilibria when (i) both the ligands are carboxylic, (ii) one of them is carboxylic and other phenolic and (iii) both the ligands are phenolic acids.

Experimental

The ligands aspartic, glutamic, thiodiglycolic, thiodipropionic, malonic, malic, 3, 5-dinitrosalicylic and 5-hydroxysalicylic acids were obtained from Fluka (Germany). These ligands were purified by repeated crystallisation and their purity was checked by their melting points. Nickel nitrate(AnalaR) was used for the preparation of metal solution and the concentration of nickel ion in the original solution was estimated by EDTA titrations[8]. The details regarding other chemicals, the experimental procedure involved in the potentiometric titration and the pH measurements are described in an earlier communication from this laboratory[9].

Results and Discussion

The dissociation constants of the ligands and the stability constants of nickel complexes were calculated by the method of Irving and Rossotti[10,11]. The presence or absence of 1 : 2 complex was established by the procedure of Ramamoorthy and

TABLE—1 LOGARITHMS OF EQUILIBRIUM CONSTANTS OF TERNARY COMPLEXES OF NICKEL ION-PRIMARY(H_2Y)-SECONDARY(H_2X) ACIDS

Temp.=30±0.1° μ=0.1M (NaClO$_4$)

Acid/Systems	β_{XY}	K_{DXY}[a]	K_{2XY}	K_{2YX}	K_{MX_2}	$\Delta \log K$
glutamic*-malonic	8.59	+0.51[b] −0.99	2.97	4.63	3.96	−0.99
glutamic-thiodiglycolic	11.26	+2.96[b] +1.40	7.08	5.64	4.18	+1.40
aspartic**-thiodipropionic	5.92	−0.95[b] −2.81	−1.20	4.31	1.61	−2.81
malic@-thiodipropionic	5.52	+0.62	3.91	2.23	3.29@	+0.62
malic-thiodiglycolic	9.02	+1.55	4.85	5.73	−	+1.55
malic-3, 5-dinitrosalicylic	7.44	+0.04	4.15	3.38	4.11	+0.04
3, 5-dinitrosalicylic-5-hydroxysalicylic	12.86	−0.65	3.46	8.75	9.40	−0.65

*$\log K_1$=5.62 ; $\log K_2$=4.12, **$\log K_1$=7.12 ; $\log K_2$=5.27.

K_{DXY}[a] = $K(MX+MY \rightleftharpoons MXY+M)$; K_{DXY}[b] = $K(MX+MY_2 \rightleftharpoons MXY+MY)$.

The accuracy of β_{XY} values was between 0.01-0.10 log units. pK values are taken from Ref. No. 7.

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* Senior author to whom all correspondence to be made.

Santappa[13]. Though the formation of mixed-ligand complex was concluded initially from qualitative evidence, Carey and Martell's[18] procedure was adopted to probe into the nature of the mixed-ligand complex and complexation equilibria. The mixed-ligand stabilities and other equilibrium constants were calculated by the procedure[14] and are set out in Table 1. All the mathematical calculations were carried out on MOSCAL 1080S SCIENTIST.

The possible complexation of mixed-ligand systems of nickel ion are given as :

$K_{MX_1} = K(M+X \rightleftharpoons MX)$,

$K_{MY_1} = K(M+Y \rightleftharpoons MY)$,

$K_{MY_2} = K(MY+Y \rightleftharpoons MY_2)$,

$K_{2XY} = K(MX+Y \rightleftharpoons MXY)$,

$K_{2YX} = K(MY+X \rightleftharpoons MXY)$ and

$\beta_{XY} = K(M+X+Y \rightleftharpoons MXY)$ must be involved.

The disproportionation constants

$K_{DXY} = K(MX+MY \rightleftharpoons MXY+M)$ and

$K_{DXY} = K(MX+MY_2 \rightleftharpoons MXY+MY)$

for corresponding systems have been calculated.

The titration curves of pH vs volume of alkali for one representative system are shown in Fig. 1. The moles of base added after the neutralization of $HClO_4$ are presented as m.

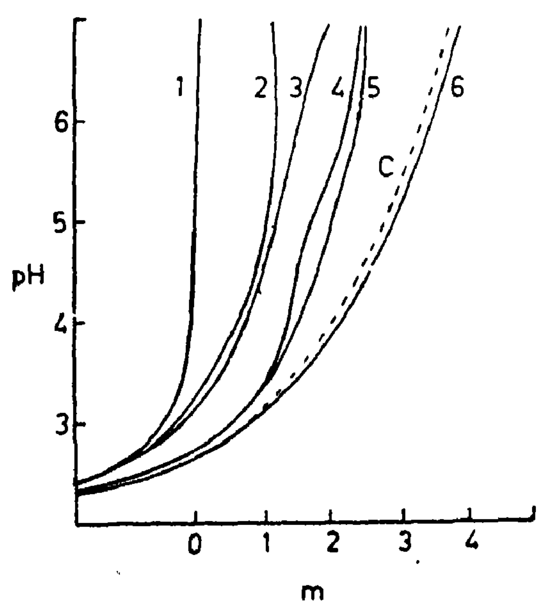


Fig. 1. Nickel ion-glutamic-malonic acid system.

$\mu = 0.1M$(NaClO$_4$), t=30°, pH titration curves of system. (i) $HClO_4$ (1), (ii) $HClO_4$+glutamic acid (2), (iii) $HClO_4$+glutamic acid+nickel ion (3), (iv) $HClO_4$+malonic acid (4), (v) $HClO_4$+malonic acid+nickel ion (5) and (vi) $HClO_4$+glutamic acid+malonic acid+nickel ion (6) against 0.38 sodium hydroxide.

c=composite curve.

Ni^{+2}-glutamic(H_2Y)-malonic(H_2X) acid system :

The pH of precipitation of mixed-ligand system was 8.9 while Ni^{+2}-malonic acid complex precipitated at 8.4. No precipitation was observed in Ni^{+2}-glutamic acid titration even up to pH 9. Glutamic acid forms both 1 : 1 and 1 : 2 complexes in the pH range 3.0-6.5. The formation of 1 : 1 with malonic acid takes place around 4.5 pH. The mixed-ligand titration curve was towards right-hand side of the composite curve in the pH range 3.5 to 5.5 at which m=1-3. The buffer region m=0-1 is due to the dissociation of first $-COOH$ group of malonic acid (pK_1=2.66). The ligand malonic acid is represented as HX^-. Since the mixed-ligand curve did not coincide with either of the individual metal titration curves, the formation of 1 : 1 : 1 complex by a simultaneous equilibrium was inferred. The complexation reaction may be represented as :

$$Ni^{+2}+HX^-+H_2Y \rightleftharpoons Ni(X)(HY)^- + 2H^+.$$

The negative $\Delta\log K$ values of ternary systems indicate that primary and secondary ligand dianions form ternary complexes preferentially to the binary ones. In the present investigation, the mixed-ligand chelates are formed by simultaneous and stepwise equilibria. In glutamic-thiodiglycolic and malic-3, 5-dinitrosalicylic acid system, the mixed-ligand chelate is formed by equilibrium :

$$K_{2XY} = K(MX+Y \rightleftharpoons MXY).$$

It is observed (Table 1) that $\Delta\log K$ values are negative for glutamic-malonic, aspartic-thiodipropionic and 5-hydroxysalicylic-3, 5-dinitrosalicylic acid systems and positive for all the remaining systems. The higher stabilities of Ni^{+2}-glutamic-malonic and Ni^{+2}-malic-thiodiglycolic than Ni^{+2}-aspartic-thiodipropionic and Ni^{+2}-malic-thiodipropionic acid systems may be ascribed to the differences in ring sizes of the chelates. In aspartic-thiodipropionic and malic-thiodipropionic acid systems, comparatively less strain involved in the ten membered ring formed by thiodipropionic acid may be responsible for the observed lower value and further confirmed by its lowest value in the binary complex ($\log K$=1.61). Though the mixed-ligand stability can be explained as due to (i) nature of donor atoms, (ii) ring size formed by the ligands, (iii) neutralization of charge in the ternary complex or (iv) steric hindrance in one of the binary complexes, our study revealed that the ring sizes formed by the two ligands are predominantly responsible for the stabilized or destabilized nature of the ternary complexes studied.

The carboxylate oxygen is not directly bound to the benzene nucleus like phenolic oxygen. The carboxylate oxygen may, therefore, adjust stereochemically more easily than the phenolate ion which is directly attached to the benzene nucleus. In the present case, greater strain in Ni–O is, therefore, expected when the phenolate oxygen is coordinated to the central metal ion when the coordination takes place through the carboxylate

oxygen. The electron affinity of the phenolate oxygen will be higher than that of carboxylate oxygen. The coloumbic repulsion between the ends oxygen will, therefore, be more when both ligands are phenolic acids than when they are carboxylate ones. Hence it is expected that the values of $\Delta \log K$ should be higher when both the ligands are phenolic than when both of them are carboxylic acids and an intermediate value is to be expected when one of them is carboxylate and other a phenolic acid. The observed value of $\Delta \log K$, in the present investigation, fit into this pattern very well.

The values of K_{DXY} run parallel to $\Delta \log K$ in all the systems for the equilibrium $MX + MY \rightleftharpoons MXY + M$. In the case of glutamic-thiodiglycolic and glutamic-malonic systems $K_{DXY} > 0.6$ log units for the equilibrium $MX + MY_2 \rightleftharpoons MXY + M$, indicates a preferential formation of ternary complexes over 1 : 2 binary complexes. The comparison of K_{MYX} and K_{MX_1} shows that the ternary complexes are more stable as compared to the binary[15,16].

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Stability Constants and Thermodynamic Functions of Trivalent Lanthanum, Cerium, Praseodymium, Neodymium and Samarium Complexes with 2-(*p*-sulphophenylazo) 1, 8-Dihydroxy naphthalene 3, 6-Disulphonic Acid (Trisodium salt) [SPADNS]

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The stepwise proton-ligand stability constants of SPADNS and its metal complexes with La(III), Ce(III), Pr(III), Nd(III) and Sm(III) have been determined potentiometrically in aqueous solution. Stability constants of these complexes were computed by Bjerrum-Calvin pH-titration technique as used by Irving and Rossotti at 20° and 40° at an ionic strength of 0.1*M* ($NaClO_4$). The trend in the stability constant values of these metal chelates has been found to be

Sm(III) > Nd(III) > Pr(III) > Ce(III) > La(III)

The values of overall changes in ΔG°, ΔH° and ΔS° accompanying complex formation have also been calculated.

A survey of the literature revealed that some studies[1-5] have been made spectrophotometrically on the complexation reactions of SPADNS with different metal ions, however, no attempt appears to have been made to evaluate the stability constant and thermodynamic parameters of Lanthanide complexes with SPADNS *p*H-metrically. In view of the above, it was considered of interest to make the study of Lanthanides-SPADNS system potentiometrically.

Experimental

The solutions of metal perchlorates were prepared by dissolving the requisite amount of metal oxides (BDH, AnalaR Grade) La_2O_3, Pr_2O_3, Nd_2O_3, Sm_2O_3 and nitrates such as $Ce(NO_3)_3$ in minimum quantities of perchloric acid. The excess of acid was removed by evaporating the solution four to five times with double distilled water. These solutions wers standardized by oxalate method[6]. The stock solutions of SPADNS (Fluka), sodium perchlorate (Riedel), perchloric acid and sodium hydroxide were prepared in the usual manner.

*p*H measurements were carried out with extended scale Phillips *p*H-meter model PR 9405 *M* with glass and calomel electrodes. *p*H-meter was calibrated using cambridge buffer tablets of *p*H 4 and 7. The titrations were carried out in an inert atmosphere of nitrogen in a specially designed double-walled beaker of capacity about 250 ml made of Pyrex glass using Calvin-Bjerrum titration technique[7,8] as modified by Irving and Rossotti[9].

Three solutions (total volume 50 ml in each case) were prepared as follows :

A : $4\times10^{-3}M$ perchloric acid, B : $4\times10^{-3}M$ perchloric acid + $3\times10^{-3}M$ ligand and C : $4\times10^{-3}M$ perchloric acid + $3\times10^{-3}M$ ligand + $5\times10^{-4}M$ metal ion solution such that the concentration of the common ingredients were identical in different cases. The ratio of the metal and ligand was always 1 : 6. An appropriate quantity of sodium perchlorate (2.0*M*) was added to maintain 0.1*M* ionic strength. The mixtures A, B and C were individually titrated against standard sodium hydroxide solution (0.4*M*).

Results and Discussion

In order to calculate the stability constants of the metal complexes, it is necessary to calculate the proton-ligand stability constants. To calculate the formation constant of the proton-ligand system, the value of $\bar{n}A$ at different *p*H values were calculated using the acid, ligand titration curves (solutions A and B) using Irving and Rossotti method[9].

A proton-ligand formation curve was then obtained by plotting the values of $\bar{n}A$ against *p*H values. The proton-ligand stability constants were obtained using the various computational techniques which are given below in Table 1.

The degree of formation of the complex ($\bar{n}$) and the negative logarithm of the free ligand concentration (*p*L) at a particular *p*H value were calculated with the help of ligand and metal titration curves (solution B & C) using Irving and Rossotti method[9].

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TABLE—1. PROTON-LIGAND STABILITY CONSTANTS OF SPADNS
0.1M ($NaClO_4$)

Method employed	TEMPERATURE 20°			40°		
	$\log K_1^H$	$\log K_2^H$	$\log \beta^H$	$\log K_1^H$	$\log K_2^H$	$\log \beta^H$
1. Interpolation of half $\bar{n}$ values[7,8]	10.85	9.15	19.50	9.65	8.65	18.30
2. Correction term method[10]	10.27	9.15	19.42	9.57	8.71	18.28
3. Least square treatment						
(a) Method of simultaneous equation[10]	10.2	9.28	19.48	9.52	8.84	18.36
(b) Curve fitting method[11]	10.28	9.07	19.35	9.67	8.60	18.28
Mean value	10.27	9.15	19.42	9.60	8.70	18.3

TABLE—2. METAL-LIGAND STABILITY CONSTANTS OF THE COMPLEXES ($\log K_1$) AND THERMODYNAMIC PARAMETERS

Metal ion	Method employed	$\log K_1$ 20°	40°	$\Delta H°$(K.cal.mol^{-1})	$\Delta S°$(cal.mol^{-1}C^{-1})
La^{3+}	A	6.95	6.70	−4.58	13.9
	B	6.95	6.77		
	C	6.95	6.70		
	Mean value	6.95	6.72		
Ce^{3+}	A	7.20	6.95		
	B	7.38	6.98	−6.86	7.6
	C	7.20	7.20		
	Mean value	7.26	7.04		
Pr^{3+}	A	7.70	7.40		
	B	7.81	7.34	−8.67	3.46
	C	7.80	7.50		
	Mean value	7.77	7.41		
Nd^{3+}	A	8.00	7.65		
	B	8.18	7.67	−9.84	0.89
	C	8.20	7.65		
	Mean value	8.13	7.66		
Sm^{3+}	A	8.60	8.25		
	B	8.55	8.30	−5.72	16.88
	C	8.60	8.30		
	Mean value	8.57	8.28		

Method A : refers to interpolation at half $\bar{n}$ values ;
B : refers to least square treatment (curve fitting) ,
C : refers to pointwise calculation method.

A metal-ligand formation curve was then obtained by plotting the values of $\bar{n}$ against pL values. The value of $\bar{n}$ does not exceed 1 in all the cases, indicating thereby the formation of only 1 : 1 complex. The values of $\log K_1$ were determined by various computational techniques which are given in Table 2. The value of $\log K_1$ was also obtained by the pointwise calculation method using the following equation :

$$\log K_1 = p\text{L} - \log (1-\bar{n})/\bar{n}$$

The values of overall changes in free energy ($\Delta°G$) enthalpy ($\Delta H°$) and entropy ($\Delta S°$) accompanying the complexation reactions have been determined applying the standard equations given below[12] :

$$\Delta G° = -\text{RT}ln\beta$$

The value of $\Delta H°$ was determined by temperature coefficient method as well as from the isobar equation

$$\frac{d ln\beta}{dT} = \frac{\Delta H°}{RT^2}$$

Assuming $\Delta H°$ to be constant over a narrow range of temperature, this can be written as

$$\frac{d(\log\beta)}{d(1/T)} = \frac{-\Delta H°}{4.576}$$

The value of $\Delta S°$ was calculated from the relation

$$\Delta S° = \frac{\Delta H° - \Delta G°}{T}$$

The values of thermodynamic parameters are given in Table 2. The values of protonation constants given in Table 1 show a decreasing tendency with increase in temperature. In all the systems the values of $\log K_1$ at 20° are greater than those at 40° indicating that the low temperature is favourable for

the complex formation. The trend in overall stability of these complexes is $Sm^{+3} > Nd^{+3} > Pr^{+3} > Ce^{+3} > La^{+3}$ at 20° and 40°. This is in accordance with the general rule that the stability of Lanthanide complexes increases with the decrease in ionic radii of Lanthanides.

The formation of Lanthanides-SPADNS complexes is spontaneous process which is evident from the more negative values of ΔG° with increase in temperature. The negative values of ΔH° ensures that the reaction is exothermic. The values of ΔS° are positive in all the cases indicating that entropy is favourable for the complex formation.

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Stability Constants of Complexes of 7-(α-*m*-nitro Anilino benzyl)-8-Quinoninol with Cu(II), Ni(II), VO(II) and Zn(II)

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The paper deals with the determination of stability constants by potentiometric method of Cu(II), Ni(II), Vo(II) and Zn(II) of the ligand m-NO_2-ABQ.

The stability constants were computed by several methods such as half integral, least squares, Linear plots, Hearon and Gilbert's and Olerup's method. They obey the Irving Williams rule. To check the validity of the results standard deviation σ was calculated.

IN continuation of our work[1,2] on 7-(α-Anilino benzyl)-8-quinolinol derivatives, the compound m-NO_2 (ABQ) was synthesized. The compound is prepared following the method of Phillips[3]. It is found to form complexes with Cu(II), Ni(II), VO(II) and Zn(II). They all form 1 : 2 complexes with this ligand.

The acid dissociation constant of the ligand was determined by half integral method and by pointwise calculation method. The stability constants are evaluated by different methods such as, half integral, least squares, linear plots Hearon and Gilberts and Olerups method. The value of standard deviation was calculated.

Experimental

It was synthesised by condensing 0.1M amine, 0.1M *m*-nitrobenzaldehyde and 0.1M 8-quinolinol in absolute alcohol to get compound(I) following the method of Phillips. It is crystallized from ethanol-acetone mixture as yellow crystals with m.p. 146°. The nitrogen and oxygen atoms of 8-quinolinol are donar atoms.

Metal solutions were prepared by dissolving metal nitrates B. D. H. AnalaR grade except vanadium for which $VOSO_4$ (B. D. H. England) was used and there solutions were prepared in double glass distilled water. The ligand solution was prepared in purified dioxane[4]. Nitric acid solution and KNO_3 solution were prepared in double distilled water.

Procedure

With a Phillips *p*H meter, and standard glass and Calomel electrodes *p*H values were measured. For *p*H measurements following solutions were prepared.

(a) ***Metal titration :*** 1 ml of 0.01*M* HNO_3+ 5ml of 1*M* KNO_3+5 ml 0.01*M* reagent solution in dioxane +7 ml of water +30 ml of pure dioxane to maintain the dioxane : water volume ratio of 70 : 30.

(b) *Reagent titration :* Same as above except that the metal salt solution was replaced by equivalent amount of pure distilled water.

(c) *Acid titration :* Same as above described under metal titration except that the metal salt solution and reagent solutions were replaced by equivalent amount of distilled and pure dioxane.

These solutions were titrated against standard alkali NaOH. The titration curves, i.e., *p*H versus volume of alkali added were plotted.

Results and Discussion

From the titration curves the average number of protons, $\bar{n}_H$ may be calculated as usual[5].

The formation curves of the proton-ligand complexes were plotted by plotting $\bar{n}_H$ against B (*p*H meter readings).

From these formation curves the pK^H is directly obtained. This is also obtained by plotting

$$\log \frac{\bar{n}_H}{1-\bar{n}_H}$$ against B to obtain a best straight line.

Thus the value is also obtained by pointwise calculations, the average value obtained by these two methods is 9.90.

The metal-ligand stability constants were also obtained by calculating $\bar{n}$ and *pL* using Irving-Rossotti method[5].

The metal-ligand stability constants can be directly read by plotting formation curves, i.e., $\bar{n}$ versus *p*L. They are also obtained by Least squares method[6], method of Linear plots[7] and Olerups method[8].

* For correspondence.

The results obtained by different methods are given in Table 1.

TABLE—1

$t=25\pm1°$ | $0.1M\ KNO_3$ | 70% dioxane

Method	I	II	III	IV	Mean		σ Standard deviation ×
Metal							
Cu(II)	10.42	9.54	10.16	9.90	9.35	$\log k_1$	
	9.90	10.55	10.02	11.24	10.42	$\log k_2$	0.051
	20.22	20.13	20.18	21.14	20.35	$\log \beta_2$	
VO(II)	9.94	9.05	10.08	9.48	9.84	$\log k_1$	
	9.48	10.44	9.39	9.82	9.68	$\log k_2$	0.095
	19.37	19.49	19.47	19.30	19.39	$\log \beta_2$	
Ni(II)	8.90	8.05	8.17	9.18	8.76	$\log k_1$	
	8.02	9.44	8.96	8.17	8.61	$\log k_2$	0.074
	17.36	17.49	17.13	17.35	17.34	$\log k\beta_2$	
Zn(II)	8.53	7.64	8.92	8.68	8.63	$\log k_1$	
	7.87	9.04	7.34	7.25	7.65	$\log k_2$	0.054
	16.40	16.68	16.76	15.93	16.34	$\log \beta_2$	

(I) Half integral, (II) Linear plots, (III) Least squares, (IV) Olerup's.

The order of stability for $\log k_1$ indicates

$$VO(II) < Cu(II) > Ni(II) > Zn(II)$$

The order of stability follows Irving-Williams rule[9]. To check the validity of the results $\bar{n}$ was recalculated using Least squares method's $\log k_1$ and $\log k_2$. The $\Delta\bar{n}$ thus obtained was used to calculate standard deviation σ^7 using the relation

$$\sigma = \pm\left[\frac{(\Sigma\Delta\bar{n})^2}{N}\right]^{\frac{1}{2}}$$

The value of σ is given in Table 1. The values of are small, i.e., the limits of errors are small in each case.

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Formation Constants of the Complexes of 2-Hydroxy-1-Naphthaldoxime with Some Trivalent Metal Ions and UO_2^{2+}

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Potentiometric studies have been carried out on metal complexes of UO_2^{2+}, Y^{3+}, Pr^{3+}, Gd^{3+}, Dy^{3+} and Nd^{3+} with 2-hydroxy-1-naphthaldoxime. The proton association constant of the reagent and the formation constants of its metal complexes have been determined by Bjerrum's method at 25°±0.1. The departure from the electrostatic bond between metal and donor atoms of the reagent has been attributed to the size of the hydrated metal ions of rare earths.

THE oxime of 2-hydroxy-1-naphthaldehyde has been reported[1] as an excellent reagent for the determination of copper in acidic solutions ; a weighable precipitate being formed without the interference from the other metal ions. Endo and Mashima[2] have used 2-hydroxy-1-naphthaldoxime as an analytical reagent for Cu. Zn, Ni and Co in acidic solution. The reagent has also been used as a volumetric reagent for Zn by Mashima[3]. Some divalent metal complexes of the reagent have been studied by Mayadeo and Kabadi[4].

In the present communication, the successive formation constants of the complexes of 2-hydroxy-1-naphthaldoxime with some rare earth ions such as Y^{3+}, Pr^{3+}, Gd^{3+}, Dy^{3+}, Nd^{3+} and divalent UO_2^{2+} have been determined potentiometrically, following the Calvin-Bjerrum *p*H titration technique as adopted by Irving and Rossotti[5].

The Corning model 12, a precision research *p*H meter with a wide range glass electrode in combination with calomel electrode system was used for *p*H measurements. The meter has an arrangement for normal and expanded scale. The smallest scale division on the expanded scale reads 0.005 *p*H unit.

Experimental

The oxime of 2-hydroxy-1-naphthaldehyde was prepared by dissolving 10 g of 2-hydroxy-1-naphthaldehyde (Fluka) in about 100 ml of 1*N* NaOH. To this solution, equimolar quantity of hydroxylamine hydrochloride was added and the reaction mixture was heated on a water bath for about half an hour. On cooling, the solution was filtered and dilute hydrochloric acid was added to the filtrate to get the oxime. It was recrystallised three times using 50 per cent. ethanol to get pure product with m.p. 158°[6].

The dioxan used for the experimental work was purified[7]. Distilled water was redistilled over alkaline potassium permanganate. This distilled water was used throughout the investigation.

The medium of titration was 75 : 25 per cent. dioxan water (v/v). Perchloric acid and sodium perchlorate were added to maintain a constant ionic strength. The titrations were carried out in an inert atmosphere by bubbling oxygen-free nitrogen through the solutions. The free acid, the free acid plus the reagent and the mixture containing metal ion, acid and the reagent were titrated separately against standard carbonate-free sodium hydroxide solution. Metal ions other than UO_2^{2+} were standardised complexometrically by EDTA titrations[8]. UO_2^{2+} was estimated by precipitating with ammonia and weighing it as U_3O_8 after igniting the precipitate in platinum crucible. All measurements were carried out at 25° ± 0.1.

The following solutions were titrated potentiometrically against standard sodium hydroxide (1.04 M).

(i) 5.0 ml $HClO_4$ (0.16 *M*)+5.0 ml $NaClO_4$ (0.64 *M*)+30 ml dioxan.

(ii) 5.0 ml $HClO_4$ (0.16 *M*)+5.0 ml $NaClO_4$ (0.64 *M*)+requisite quantity of the reagent to give 0.004 *M* reagent concentration in the final solution+30 ml dioxan.

(iii) 5.0 ml $NaClO_4$ (0.64 *M*)+5.0 ml metal salt (0.008 *M*) in 0.16 *M* $HClO_4$+the reagent as in *(ii)* above+30 ml dioxan.

The computational method of Irving and Rossotti[5] was applied to calculate $\bar{n}$ and *p*L values.

Results and Discussion

In the reagent, it is the phenolic "OH group" which takes part in complex formation and the proton is replaced from it by metal ion during the formation of metal chelate. Since only one proton per reagent molecule is liberated during complexation, 'Y' the number of dissociable protons attached to each ligand molecule is one.

From the titration curves obtained with the solutions (i) and (ii), $\bar{n}_A$ values at various 'B' values (pH meter readings) were evaluated. A curve between 'B' and the corresponding $\bar{n}_A$ values was plotted from which the value of practical proton association constant log $^{P}K^{H}_{OH}$ was calculated by half integral method which corresponds to 'B' value at $\bar{n}_A$ equal to 0.5. Log $^{P}K^{H}_{OH}$ was also evaluated using the formation function

$\log \frac{\bar{n}_A}{1-\bar{n}_A} = \log {}^{P}K^{H}_{OH} - B$; and selecting the points through $\log \frac{\bar{n}_A}{1-\bar{n}_A}$, B plots. The two values agree quite well.

From the titration curves of solutions (ii) and (iii), $\bar{n}$ and pL values were calculated. $\bar{n}$ values were plotted against the corresponding pL values to get the formation curves of the metal complex equilibria. From these formation curves, the values of metal ligand formation (stability) constants, $\log K_1$ and $\log K_2$ were evaluated which correspond to pL values at $\bar{n}=0.5$ and $\bar{n}=1.5$ respectively.

In the case where formation curves were incomplete, the constants corresponding to 1 : 1 metal legand complexes were evaluated by using the formation function

$$\log \frac{\bar{n}}{1-\bar{n}} = \log K_1 - pL$$

while in the case of 1 : 2 complexes the formation function used is

$$\log \frac{\bar{n}-1}{2-\bar{n}} = \log K_2 - pL$$

Therefore, selection of points were made through $\log \frac{\bar{n}}{1-\bar{n}}$, pL plot for evaluation of $\log K_1$ and $\log \frac{2-\bar{n}}{\bar{n}-1}$, pL plots for $\log K_2$. The most representative values are recorded in Table 1.

TABLE—1

STEPWISE STABILITY CONSTANTS OF VARIOUS COMPLEXES

t=25° $\mu=0.1M$

Cations	H^+	Y^{3+}	Pr^{3+}	Gd^{3+}	Dy^{3+}	Nd^{3+}	UO_2^{2+}
$\log K_1$	11.84	8.24	7.78	8.57	8.89	8.35	11.30
$\log K_2$	–	7.35	–	–	7.56	–	9.61

The values of formation constants reported in Table 1 were determined for the first time in 75 : 25 dioxan-water (v/v) medium. The order of stability of trivalent metal chelates is found to be

$$Dy^{3+} > Gd^{3+} > Nd^{3+} > Y^{3+} > Pr^{3+}$$

In the case of rare earth complexes, the absence of extensive covalent bonding is indicated by non-availability of 4 f electrons for bond formation due to their shielding by 5 s and 5 p electrons and also their large crystal radii ranging from 0.85 to 1.06Å. If ionic bonding exists, there shall be increase in stabilities of rare earth complexes with decreasing ionic or crystal radii and according to Born equation, a correlation should exist between metal ligand stability and e^2/r or e/r (where e = charge of gaseous metal ion and r = radius of the ion).

In the present investigation it is seen from the Table 1 that the values of stability constants of rare earth complexes are not as expected from the above consideration, but show marked deviation. Such deviations as suggested by some workers[9] may be due to varying degree of stabilisation arising out of interaction of 4 f metal orbitals with the ligand field.

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Acid-Catalyzed Dissociation of Cobalt(III) Chelates I. Aquation Kinetics of *Cis*-Diaquobisbiguanide-cobalt(III) Perchlorate

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The kinetics of the acid-catalyzed dissociation of *cis*-diaquo*bis*biguanidecobalt(III) complex ion was made spectrophotometrically in the temperature range 50°-65° in presence of 0.3 to 2.0 M perchloric acid. The second order rate constants (k') at various temperatures were evaluated from the slopes of the lines obtained by plotting k_{obs} vs $[HClO_4]$. The enthalpy and entropy of activations were determined in the usual manner and the values were found to be $\Delta H^{\ddagger} = 15.2 \pm 0.7$ k cals mol^{-1} and $\Delta S^{\ddagger} = -31.6 \pm 2.1$ e.u. Kinetically the *bis*-complex is more stable than its *tris*-analogue. A dissociation mechanism was proposed for the aquation reaction.

STEPWISE dissociation of cobalt(III)-biguanide complex in acid solution is well established[1]. *Tris*-biguanidecobalt(III) complex ion aquates[2] at a measurable rate in acid solution with the formation of diaquo*bis*biguanide complex. This diaquo-complex further dissociate to tetraaquo*mono*-biguanide complex and spontaneously decomposes to cobaltous ion with simultaneous release of biguanides. In this paper, the dissociation of diaquo*bis*biguanidecobalt(III) ion to tetraaquo-*mono*biguanidecobalt(III) ion in aqueous acidic medium is reported as a function of acid concentration, ionic strength and temperature.

Experimental

Materials and reagents :

Diaquo*bis*biguanidecobalt(III) perchlorate—Hydroxoaquo*bis*biguanidecobalt(III) sulphate was prepared by the method of Ray and Ghosh[3]. Its purity was checked by analysis (Found : Co, 13.44 ; N, 32.60 per cent. Calcd, for $[Co(BigH)_2(OH)(H_2O)]SO_4.2.5H_2O$: Co, 13.50 ; N, 32.04 per cent.). A solution of the complex perchlorate was prepared before use by metatheses of the complex sulphate with an equivalent amount of barium perchlorate. It is known[3] that the hydroxoaquo-complex in aqueous solution forms an equilibrium mixture with the diaquo-complex. The *p*K value for the reaction $[Co(BigH)_2(OH)(H_2O)]^{2+} + H_3O^+ \rightleftharpoons [Co(BigH)_2(H_2O)_2]^{3+} + H_2O$ was determined at various temperatures (30° – 50°) by the *p*H titration of the complex perchlorate with perchloric acid as 6.02 at 2*M* ionic strength. So in the experimental acid concentrations (0.3*M*-2.0*M*), the complex ion exists entirely as the diaquo species. The formation of the diaquo-species is also evident from the immediate shift in the absorption maxima of $Co(BigH)_2(H_2O)(OH)^{2+}$ from 480 nm to 490-495 nm by the addition of acid to an aqueous solutions of the latter. The absorption spectrum of the complex ion in 1*M* perchloric acid is shown in Figure 1.

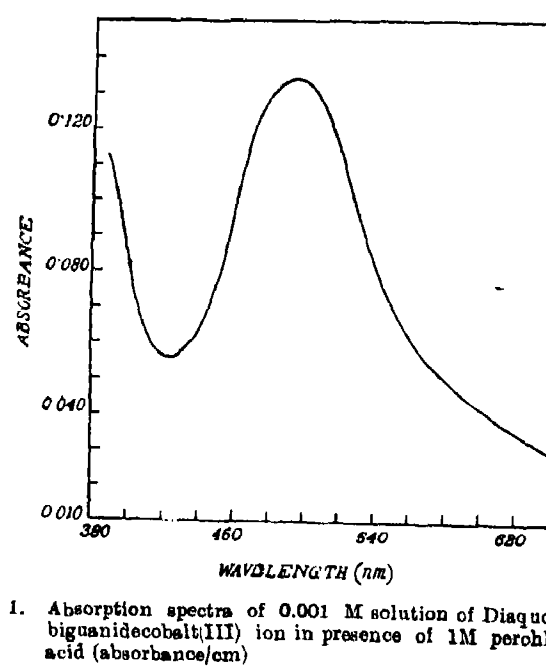


Fig. 1. Absorption spectra of 0.001 M solution of Diaquo*bis*-biguanidecobalt(III) ion in presence of 1M perchloric acid (absorbance/cm)

Kinetic measurements :

The rates of reactions were followed spectrophotometrically in the same way as had been done with *trans*-dicyano*bis*-biguanidecobalt(III) ion[4]. The absorbance measurements were made at 490 nm,

corresponding to the absorption peak of the diaquo-complex, where a maximum change in absorption occurs. The rates were evaluated by Guggenhiems' plot[5], as it was difficult to ascertain the absorption due to pure tetraaquo-complex.

Results and Discussion

The observed rate of dissociation of the complex ion at various complex and acid concentrations and different temperatures are reported in Table 1. The values given in the table are average of two or three individual runs and the rates are reproducible within three per cent. The rate of dissociation of the diaquo-complex remains unchanged with different initial amounts, indicating a first order dependence of rate on complex concentration. k_{obsd} changes with acid concentration. Plot of k_{obsd} *vs* $[HClO_4]$ (Figure 2) at various temperatures are straight lines with zero intercept on ordinate. This indicates that the dissociation of the complex proceeds only through an acid-catalyzed path with virtually no contribution by any acid independent path. The straight line plot also indicates first order dependence of rate on acid concentration. From the slopes of these plots, the second order rate constant, k', for the dissociation of the complex at various temperatures were determined and are also reported in Table 1. Corresponding theoretical rate law may be derived as :

TABLE—1

OBSERVED RATES FOR THE ACID-CATALYZED DISSOCIATION OF DIAQUO*bis*BIGUANIDECOBALT(III) PERCHLORATE AT VARIOUS ACID CONCENTRATIONS AND TEMPERATURE, $\mu = 2.0M$

Complex × 10^{-3} M	$HClO_4$, M	$10^3 k_{obsd}$ min^{-1} 55°	60°	65°
1	0.3		2.16	
2	0.3		2.21	
3	0.3		2.17	
1	0.5	2.10	2.90	4.34
1	0.7	3.78	5.16	6.14
1	1.0	4.30	6.90	9.01
1	1.2	5.00	8.44	
1	1.5		10.60	
1	2.0		12.50	
$10^3 k'$ min^{-1} (second order rate constant)		4.3	6.95	8.95
$10^5 k'$ sec^{-1} „ „		7.2	10.16	10.49

$\Delta H^{\ddagger} = 15.2 \pm 0.7$ *k* calories mol^{-1} $\Delta S^{\ddagger} = -31.6 \pm 2.1$ e.u.

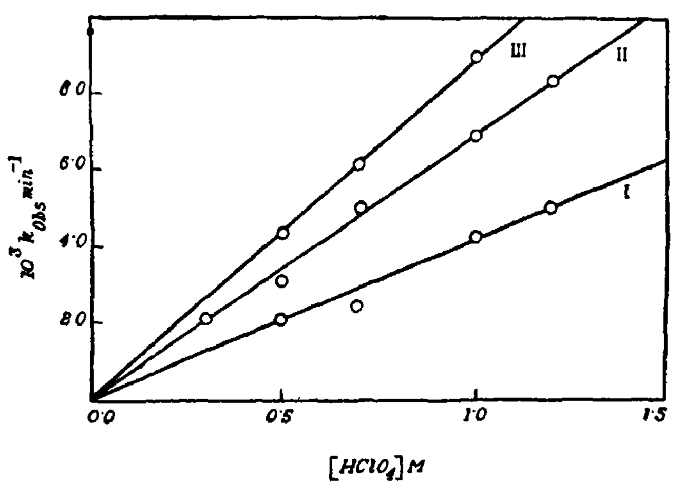


Fig. 2. Effect of acid concentration on the rate of dissociation of Diaquobisbiguanidecobalt(III) ion at various temperatures (μ, 2)
I—55° ; II—60° ; III—65°.

$$-\frac{d}{dt} \ln [Co(BigH)_2(H_2O)_2^{3+}] = k_{obsd} = k'[H^+] \quad ...(1)$$

Based on the above rate law, the mechanistic path of the dissociation may be given as :

$$(H_2O)_2Co(BigH)_2^{3+} + H \underset{\text{instantaneous}}{\overset{K}{\rightleftharpoons}}$$

$$(H_2O)_2Co(BigH)(BigH_2)^{4+} \underset{\text{slow}}{\overset{2H_2O}{\longrightarrow}}$$

$$(H_2O)_2Co(BigH)(H_2O)_2^{3+} + BigH_2^{+}$$

(BigH = biguanide, $C_2N_5H_7$)

The equilibrium constant '*K*' is assumed to be small, so that the concentration of the conjugate acid at any time is very small in comparison with the complex. Protonation takes place at the free basic=NH group of the cobalt bound biguanide molecule.

The effect of ionic strength on the rate is shown in Table 2. Rate increases but little with ionic strength. Whether the rate increases with ionic strength or perchlorate concentration, was tested by using mixtures of sodium and barium perchlorates for maintaining different ionic and perchlorate concentrations. No remarkable effect of perchlorate concentration on the rate was observed, although the rate increases with ionic concentration.

TABLE—2

EFFECT OF IONIC CONCENTRATION AND PERCHLORATE CONCENTRATION ON THE RATE OF AQUATION OF DIAQUO*bis*BIGUANIDECOBALT(III) ION

Complex——0.001M, Temp. 60°

	$HClO_4$,M	$NaClO_4$,M	$Ba(ClO_4)_2$,M	μ	$[ClO_4^-]$	$10^3 k_{obs}$ min^{-1}
1	1.0	1.0		2.0	2.0	6.91
2	1.0	0.5		1.5	1.5	5.70
3	1.0			1.0	1.0	4.74
4	1.0		0.66	2.0	2.32	6.72

The heat, $\Delta H^{\ddagger}$ and entropy, $\Delta S^{\ddagger}$ of activation for the second order rate constant, k', were evaluated by making use of the Eyring equation, $\log \frac{k'h}{KT} = \frac{\Delta S^{\ddagger}}{4.6} - \frac{\Delta H^{\ddagger}}{4.6T}$ (Figure 3) where '*h*' is Planck's constant, '*K*' is the Boltzmann constant

and 'k'' is the second order rate constant for the dissociation of the complex ion. The $\Delta H^{\ddagger}$ value thus obtained is 15.2 ± 0.7 k cals mol^{-1} and $\Delta S^{\ddagger} = -31.6 \pm 2.1$ e.u. $\Delta H^{\ddagger}$ for the dissociation of the *bis*biguanide complex is higher than the corresponding value of the *tris*biguanidecobalt(III) ion[2], indicating that the *bis*complex is kinetically more stable than the *tris*-complex. This is a general behaviour observed with other biguanide complexes[3]. The thermodynamic stability of the *bis*-complex is also much higher than the *tris*-complex showing stronger bonding in the previous one.

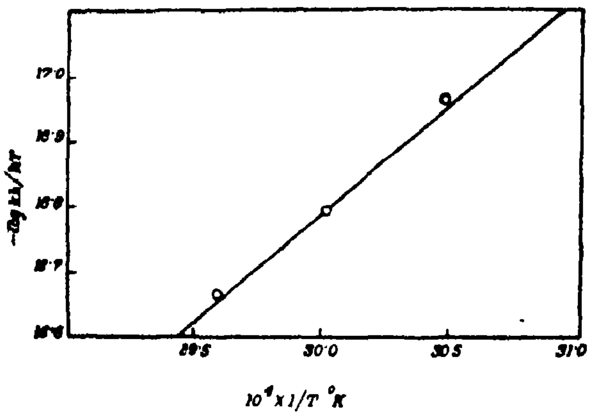


Fig. 3. Eyring plot for the dissociation of Diaquo*bis*biguanidocobalt(III) complex.

In the case of ligands which are better coordinated than water, the replacement of the ligand (in this experiment, it is biguanide) by water increases the effective positive charge on the metal atom due to weaker donation of electrons from the aquo ligand, compared to that from the ligand being replaced. The rupture of the cobalt-biguanide bond becomes increasingly difficult with increase in the effective positive charge on the cobalt atom and hence the decrease in rate occurs as observed with aquo complexes. As for example, it may be cited that while the *tris*-biguanidecobalt(III) perchlorate dissociates at a measurable rate ($48 \times 10^{-3} min^{-1}$ at 27°) at room temperature in presence of 0.1M $HClO_4$, the diaquo*bis*biguanide complex is almost stable at room temperature even in presence of 1M perchloric acid.

In this connection it may also be mentioned that $Co(en)_2(H_2O)_2^{3+}$ and $Co(mal)_2(H_2O)_2^-$, (where en = enthylenediamine, and mal = malonate) are much more reactive than their *tris*-analogues. $Coen_3^{3+}$ is perfectly stable at 80° in presence of 1M perchloric acid but $Coen_2(H_2O)_2^{3+}$ reacts at a measurable rate[6] ($k = 1.5 \times 10^{-10}$ M^{-1} sec^{-1}) under the same conditions. Also while Co $(mal)_3^{3-}$ reacts at a measurable rate at 25° and 0.1M $HClO_4$, $Co(mal)_2(H_2O)_2^-$ is extremely labile under the same conditions[7]. In cobalt(III)-biguanide complexes, the observed opposite trend indicated by the greater reactivity of the *tris*-complex, indicates a different mechanism altogether. While in the former complexes, 'bond breaking' and 'bond making' by the incoming aquo ligands are both important in the transition state[6,7], in biguanide complexes it seems that 'bond breaking' is only important. The entropies of activation of *tris*-($\Delta S^{\ddagger} = -31.5$ e.u.)[2] and *bis*-($\Delta S^{\ddagger} = -31.6$ e.u) complexes are almost equal indicating similar mechanisms operate in the aquation of both complex.

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Extraction Studies of Niobium(V) with n-*m*-Tolyl-*p*-Methoxy-benzohydroxamic Acid (TMBHA)

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The present communication deals with the various aspects of Nb(V)—TMBHA extraction studies in water-chloroform system. In 1-8 *M* hydrochloric acid medium, this reagent forms a greenish-yellow coloured complex with niobium(V) which can be extracted into chloroform. The composition of the complex is found to be 1 : 2 with respect to niobium and reagent (TMBHA). The stepwise conditional stability constants of this complex also have been determined by Yatsimirskii's and Leden's methods.

RECENTLY N-*m*-tolyl-*p*-methoxybenzohydroxamic acid (TMBHA) has been used for the solvent extraction and spectrophotometric determination of vanadium(V)[1]. This reagent has been found to form coloured chelates with various metal ions[2]. The extraction studies of niobium(V) with this reagent (TMBHA) has not been carried out so far and hence it is undertaken for the first time in this laboratory.

Experimental

Apparatus and Reagents

Standard niobium solution was prepared in tartaric acid[3]. The niobium content was estimated gravimetrically with 8-hydroxyquinoline[4].

The reagent (TMBHA) was synthesised by the method as described by earlier workers.[5] Fresh solutions of the reagent in distilled chloroform were used.

A Beckman DU-2 spectrophotometer with 1 cm quartz cells was used for spectrophotometric measurements.

General Procedure :

An aliquot of niobium solution containing 2-20 μg of Nb(V) was taken and to it added enough concentrated hydrochloric acid so as to make acid strength in the range 1-8*M*. The total volume of aqueous phase was made to 10 ml with distilled water. Aqueous phase was equilibrated with 10 ml of reagent solution in chloroform for 10 min. The absorbance of the extracted complex was measured at 320 nm against the similarly processed reagent as a blank. The amount of Nb extracted was computed from the calibration curve.

Results and Discussion

Spectral Properties

It is shown in Figure 1 that reagent (TMBHA) has an absorption maximum at 255 nm ($\epsilon = 1.5 \times 10^4$) and the greenish-yellow coloured complex at 320 nm ($\epsilon = 2.15 \times 10^4$). The system obeys Beer's law within the concentration range of 0.02 to 4.0 μg Nb(V) ml^{-1} of chloroform. The effective working range was found to be 0.8-2.5 μg Nb(V) ml^{-1} of chloroform by Ringbom curve. The Sandell's sensitivity of the complex at 320 nm is 0.0043 μg/cm..[2] The complex is stable for 24 hrs.

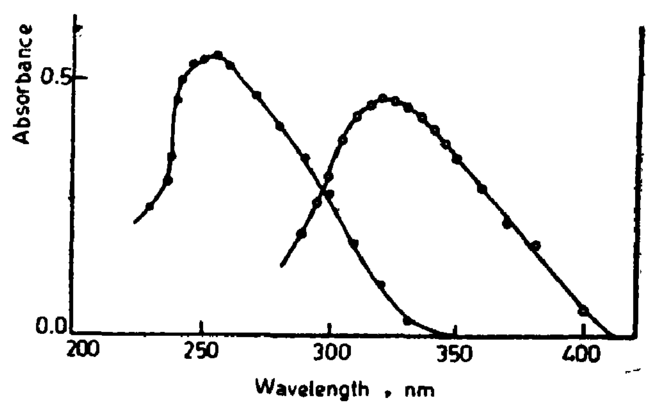


Fig. 1. Absorption spectra of Nb(V)-TMBHA complex.
○ - - - ○ Complex against reagent blank— Nb(V) = 4.0×10^{-5} *M*
● - - - ● reagent blank against Chloroform TMBHA = 3.7×10^{-5} *M*

Effect of concentration of acid and $MgCl_2$

The extent of Nb (15 μg) extraction increases with the increase in concentration of hydrochloric acid within the range of 1.0 to 8.0*M*. The effect of increasing $MgCl_2$ concentration (3.0 to 8.0*M*) at fixed hydrochloric acid concentration (2.5*M*) also shows the increase in the extent of Nb extraction. The extraction was also studied at fixed ionic strength (4.0*M* $MgCl_2$) and different hydrogen ion concentration. The results reveal that extraction is also a function of hydrogen ion concentration. The

values of per cent extraction (%E) and distribution ratio (D) at various acidity are given in Table 1.

TABLE 1

EXTRACTION OF Nb(V)-TMBHA COMPLEX AS A FUNCTION OF HYDROCHLORIC ACID CONCENTRATION, Nb(V) = 15 μg; [TMBHA] = $1.6 \times 10^{-3} M$ IN CHLOROFORM

Molarity of HCl	Per cent. extraction %E	Distribution ratio D
1.0	13.58	0.1572
2.0	17.60	0.2137
3.0	23.20	0.3022
4.0	37.60	0.6028
4.5	52.01	1.0838
5.0	75.18	3.0307
5.5	90.40	9.4249
6.0	95.19	19.79
7.0	96.02	24.03
8.0	98.40	61.3729
9.0	98.40	61.3729

Effect of reagent concentration

Niobium (15 μg) was extracted with different concentrations of reagent varying from 4.0×10^{-5} to $2.0 \times 10^{-3} M$. The per cent. extraction varies between 7.0 to 98.0% within the concentration range of 4.0×10^{-5} to $1.6 \times 10^{-3} M$ reagent and remains constant thereafter. Therefore $1.6 \times 10^{-3} M$ reagent was used for extraction.

Effect of solvents

Amongst the several solvents tried (benzene, carbon tetrachloride, isoamyl alcohol, isobutanol and chloroform), chloroform was preferred because of high sensitivity of reagent in it and its high extractability towards Nb-complex. The absorbance values for the solvents given above are 0.500, 0.490, 0.310, 0.480 and 0.550 respectively.

Time of equilibrium

The aqueous phase was equilibrated from 1 to 30 min. The per cent. extraction for times 1, 2, 3, 4 and 5 min is 64, 75, 90, 95 and 98 respectively. However, after 5 min, per cent. extraction remains constant and hence a time of 10 min was arbitrarily chosen for entire extraction studies.

Effect of diverse ions

Most of the associated cations do not interfere with the determination of Nb(V) in large excess—Fe^{3+}, Mn^{2+}, ZrO^{2+}, Co^{2+}, Cd^{2+}, Ba^{2+}, Hg^{2+}, VO^{2+}, UO_2^{2+}, and Ni^{2+} can be tolerated in more than 100 times excess. About 25 times excess Ta^{5+} can be tolerated. The most interfering cations are Ti^{4+}, $Mo_7O_{24}^{6-}$, WO_4^{2-}, V^{5+}, and Sn^{2+}. Of the various anions and complexing agents, F^- interferes seriously. Br^-, I^-, SO_4^{2-} SO_3^{2-}, $S_2O_8^{2-}$, BO_3^{3-}, PO_4^{3-}, can be tolerated in large excess. Citrate, acetate, and EDTA do not interfere. About 800 times excess oxalate can be tolerated.

From ten determinations with 15 μg of niobium the absorbance was found to be 0.460 ± 0.010 at 320 nm. Average and maximum relative deviation were found to be 0.52% and 0.74% respectively. The total operation requires about 30 min.

Composition of the extractable species

The fact that the extraction is dependent on acid, reagent and $MgCl_2$ concentration, indicates the important role of all these factors in the formation of extractable species.

By varying the hydrochloric acid concentration from 1.0 to 8.0M its distribution ratio $D_{(Nb)}$ dependence indicates liberation of two protons in the extraction system.

A plot of log $D_{(Nb)}$ versus log$[H^+]$ at fixed chloride ion concentration (8.0M) gives a slope of two. Similarly a plot of log $D_{(Nb)}$ versus log $[Cl^-]$ at fixed $[H^+]$ (2.5M) shows a slope of two. These observations clearly show the liberation of two protons and two chloride ions in the reaction.

The extraction reaction therefore, can be written as :

$$NbOCl_{3_{aq}} + 2HR \rightleftharpoons NbOClR_{2_{org}} + 2H^+ + 2Cl^-$$

where, HR = TMBHA.

Thus, the probable extractable species might be $NbOClR_2$. The stoichiometric ratio of Nb : HR for the formation of extractable neutral complex of fixed hydrochloric acid concentration (2.5M) and 5.0M chloride ion concentration has been observed to be 1 : 2. This composition is supported by Job's[6] method as applied by Kabadi[7] for liquid-liquid extraction studies and mole ratio[8] method. This composition has further been confirmed by a plot of log $D_{(Nb)}$ versus log $[TMBHA]_{org}$ (concentration of TMBHA in organic phase at equilibrium) which gave a slope of two.

Metal-ligand stability constants

The conditional metal ligand stepwise stability constants of the extracted complex were computed from the spectrophotometric data by Yatsimirskii's[9,10] and Leden's[11] methods. The values of stability constants by these methods are found to be $\log K_1 = 3.99$, $\log K_2 = 3.51$ by Yatsimirskii's method and $\log K_1 = 4.02$, $\log K_2 = 3.32$ by Leden's method.

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Separation of Bi(III) by Anion-Exchange Chromatography in Maleate and Succinate Solutions†

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Systematic studies on the anion-exchange behaviour of Bi(III) in maleic acid and succinic acid solutions on Amberlite IRA-401 are carried out. Sulphuric, nitric and perchloric acids at different concentrations were tried as eluants in the two systems. Their efficiency being evaluated in terms of distribution coefficients. Methods have been developed for the separation of Bi(III) from several elements in maleate as well as in succinate media with the technique of selective sorption or selective elution. Methods are applied to the analysis of Wood's metal. Separations are also worked out with liquid anion-exchanger, Amberlite LA-I in xylene.

ION-EXCHANGE behaviour of Bi(III) has been extensively studied in mineral acid media as both anionic and cationic complex[1-3]. However, in carboxylic acid media the studies are mainly confined to cation exchange separations[4,5]. Although for anion exchange separations, limited use has been made of EDTA[6], oxalate[7,8] and formate[9], no work has been reported on the ion-exchange behaviour of Bi(III) in maleic acid and succinic acid solutions. Present work relates to the systematic study of the ion-exchange separation of Bi(III) on Amberlite IRA-401 from several elements in maleate and succinate media. Liquid anion-exchanger, Amberlite LA-I, is also used for the separation of Bi(III) from various elements.

Experimental

Apparatus and reagents : An anion-exchange column (1×7 cm) was used. A Toshniwal *p*H meter was used for *p*H measurements.

A stock solution of Bi(III) was prepared by dissolving 1-16 g of A. R. bismuth nitrate pentahydrate in dilute nitric acid and making up to 500 ml with double distilled water. The solution on standardisation volumetrically[10] with EDTA contained 0.93 mg ml^{-1} of Bi(III).

EDTA (0.01 M) was prepared in double distilled water. The ion-exchangers used are Amberlite IRA-401 (Cl^-) and Amberlite LA-I (both from Robm and Hass Company, Philadelphia, U.S.A.). The resin was converted to the appropriate form by equilibrating for 6 hrs. with a 2% solution of maleic acid or succinic acid. The resin was then washed free of the excess acid using double distilled water.

Results and Discussion

Ion-exchange studies in maleate and succinate media : The distribution coefficients (Kd values) of Bi(III) and other related metals like Pd^{2+}, Cd^{2+}, In^{3+}, Zn^{2+}, Mg^{2+}, Co^{2+}, Ni^{2+}, Th^{4+}, etc., were determined by equilibrating 2.5 g of resin (maleate form) with 10 ml of about 1 mg. ml^{-1} solutions of metals and 20 ml maleic acid at different concentrations. The metal present in the aqueous phase was

TABLE—1. Kd VALUES IN MALEIC AND SUCCINIC ACIDS

Metal	Maleic acid, %					Succinic acid, %				
	0.50	1	2	4	6	0.50	1	2	4	6
Bi	117.60	117.80	119.00	118.00	118.00	146.90	140.00	136.00	140.00	140.20
Th	0.60	0.60	0.62	0.61	0.61	75.40	38.40	17.60	4.50	7.90
Fe	0.90	0.90	0.90	0.90	0.90	0.45	0.62	0.62	0.43	0.45
Pb	0.77	0.76	0.76	0.77	0.76	0.25	0.29	0.29	0.29	0.29
Zn	0.17	0.17	0.17	0.17	0.17	N.A	N.A	N.A	N.A	N.A
Cd	1.16	1.60	1.80	1.80	1.60	0.59	0.59	0.50	0.59	0.50
Co	0.16	0.16	0.16	0.16	0.16	0.49	0.49	0.49	0.58	0.58
Ni	N.A	N.A	N.A	N.A	N.A	0.63	0.63	0.63	0.63	0.60
In	0.62	0.62	0.62	0.62	0.62	N.A	N.A	N.A	N.A	N.A
Mg	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A
Mn	0.29	0.29	0.29	0.10	0.10	0.36	0.36	0.39	0.39	0.39

N.A = No Absorption.

† The paper was presented at the Annual Convention of Chemists, Bangalore, 1976.

determined volumetrically by EDTA[11]. K_d values are calculated and results given in Table 1.

K_d values of metals in succinic acid was also determined in a similar manner by taking the succinate form of the resin. Sulphuric, nitric and perchloric acids at different concentrations were tested as eluants, their efficiency being evaluated in terms of distribution coefficients which are given in Table 2.

In maleic acid, as seen from Table 1, there is a large difference in the K_d values between Bi(III) and other metals thereby indicating the possibilities of good separation of Bi(III) from other metals. For the elution of Bi(III) from the resin, various eluants were tried. The anionic maleate complex of Bi(III) was sorbed on the column. After washing the column with 20 ml distilled water, Bi(III) was eluted with various eluants. Collected 10 ml fractions of the effluent and analysed for the metal content using EDTA.

The elution constant (E) and the volume distribution coefficient (D_v) were calculated[12] from the peak elution volume (V_{max}) and total volume of the eluants (Vt). The results are shown in Table 3. On the basis of the results, the eluants can be arranged in the order of increasing efficiency as follows :

$$NaNO_3 < HCl < HNO_3 < HClO_4 < H_2SO_4$$

Ammonium sulphate, ammonium chloride and sodium chloride are found to be poor eluants.

In succinic acid medium (Table 1) both Bi(III) and Th(IV) show considerable sorption and these two can be separated from each other by selective elution by mineral acids ; while all other metals are sorbed very little and can be separated by selective sorption.

Elution studies of the anionic succinate complex of Bi(III) was done as described for maleic acid complex and the results are incorporated in Table 3. Here also eluants showed nearly the same order of increasing efficiency

$$HNO_3 < HCl < HClO_4 < H_2SO_4$$

Other eluants such as ammonium sulphate, ammonium chloride and sodium nitrate do not elute satisfactorily.

Separation in maleate medium : The separation of Bi(III) from Pb^{2+}, Cd^{2+}, In^{3+}, Co^{2+}, Zn^{2+}, Ni^{2+},

TABLE—2 : K_d VALUES IN NITRIC, PERCHLORIC AND SULPHURIC ACIDS

Metal	Nitric acid			Perchloric acid			Sulphuric acid		
	1N	2N	3N	1N	2N	3N	1N	2N	3N
Th	0.37	0.37	0.37	N.A	N.A	N.A	5.02	5.07	5.08
Fe	N.A	N.A	N.A	1.88	2.52	2.52	1.08	1.08	1.08
Bi	92.10	92.00	92.00	10.79	6.99	5.14	N.A	N.A	N.A
Pb	0.77	0.77	0.77	N.A	N.A	N.A	2.87	2.90	2.87
Zn	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A
Cd	8.36	8.36	8.36	5.45	5.40	5.45	N.A	N.A	N.A
Co	N.A	N.A	N.A	N.A	N.A	N.A	0.18	0.20	0.18
Ni	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A
In	0.03	0.03	0.01	N.A	N.A	N.A	N.A	N.A	N.A
Tl	0.14	0.14	0.14	N.A	N.A	N.A	0.17	0.16	0.16
Mg	N.A	N.A	N.A	N.A	N.A	0.18	N.A	N.A	N.A
Mn	0.09	0.09	0.09	0.09	0.09	0.08	0.09	0.91	0.87

N.A = No absorption

TABLE—3 : ANION-EXCHANGE STUDIES OF BISMUTH

Eluant	Concentration N	Peak elution volume V_{max}		Total volume of eluant Vt		% Recovery		Elution constant E		Volume distribution coefficient D_v	
		Maleic	Succinic	Maleic	Succinic	Maleic	Succinic	Maleic	Succinic	Maleic	Succinic
H_2SO_4	1.0	20	20	50	50	100.00	100.00	0.08	0.08	4.09	4.09
	2.0	20	10	40	40	100.00	100.00	0.10	0.10	4·09	2.04
	3.0	10	10	20	20	100.00	100.00	0.19	0.19	1.54	2.04
HNO_3	1.0	–	–	120	200	55.00	54.00	0.03	0.02	–	–
	2.0	50	60	80	180	58.50	58.80	0.04	0.03	11.74	–
	3.0	40	–	60	120	60.50	60.00	0.06	0.03	10.10	–
HCl	1.0	–	–	150	150	62.50	60.00	0.03	0.03	–	
	2.0	–	–	120	120	64.00	64.50	0.03	0.03	–	–
	3.0	60	50	110	80	65.00	70.50	0.04	0.05	7.64	14.79
$HClO_4$	1.0	50	–	80	120	78.40	70.80	0.04	0.03	11.74	–
	2.0	30	60	60	80	80.60	72.20	0.06	0.05	7.64	14.79
	3.0	20	30	50	60	84.00	84.00	0.07	0.06	4.09	7.64
$NaNO_3$	1.0	–	–	160	–	56.50	–	0.03	–	–	–
	2.0	–	–	140	–	58.00	–	0.03	–	–	–
	3.0	–	–	130	150	60.10	54.60	0.03	0.03	–	–
$NaClO_4$	1.0	–	–	200	–	65.00	–	0.02	–	–	–
	2.0	–	–	150	200	70.80	65.00	0.03	0.02	–	–
	3.0	–	–	120	150	74.50	72.00	0.03	0.03	–	–

Fe^{3+}, Mg^{2+}, Mn^{2+} and Th^{4+} was based on selective sorption. *Bi(III)* forms strong anionic maleate complex at *pH* 2-3 and it is absorbed in the column ; while other metals are not retained on the column when sorbed along with Bi(III).

Binary mixtures of Bi(III) with other metals containing sufficient amount of maleic acid (2%) was loaded on a column of anion exchange resin (2.5 g). The solution was recycled thrice at a flow rate of 1 ml min^{-1} and was kept for 30 min. The effluent was collected and the resin washed with some distilled water and Bi(III) was then eluted with $2N$ H_2SO_4. The results are given in Table 4.

TABLE – 4

SEPARATION OF Bi(III) IN MALEATE AND SUCCINATE, MEDIA, Bi(III) = 9.3 MG

Foreign ion	Amount added	Maleate medium: Bi recovered mg	Maleate medium: Per cent. recovery, %	Succinate medium: Bi recovered, mg	Succinate medium: Per cent. recovery, %
Th	7.56	9.30	100 00	9.30	100.00
In	9.59	9.30	100.00	9.30	100.00
Zn	8.40	9.30	100 00	9.00	99.17
Fe(III)	7.42	8.74	94.60	9.30	100.00
Ni	7.00	9.15	99.00	9.30	100.00
Co	7.00	9.30	100.00	8.70	93.54
Mn	7.00	9.30	100.00	9.30	100.00
Mg	6.86	9.82	105.00	Precipitation	
Pb	6.83	9.30	100.00	8.70	93.54
Cd	7.70	9.30	100.00	8.40	90.40

A similar separation was possible using the liquid anion-exchanger, Amberlite LA-1 (Table 5). A few drops of $1M$ NH_4Cl was added to the aqueous phase for clear separation of layers. For experimental work 15 ml of 2% maleic acid (or succinic acid) and 20 ml of 10% Amberlite LA-1 in xylene were used. Bi(III) was back-extracted from the organic phase using two 10 ml portions of $2N$ H_2SO_4.

TABLE -5

LIQUID ANION-EXCHANGE SEPARATION OF Bi(III) IN MALEATE AND SUCCINATE MEDIUM, Bi = 5.40 MG

Foreign ion	Amount added, mg	Maleate medium: Bi recovered mg	Maleate medium: Per cent. recovery %	Succinate medium: Bi recovered mg	Succinate medium: Per cent. recovery, %
Th	3.20	5.40	100.00	5 40	100.00
In	4.13	5.40	100.00	5.40	100.00
Ni	3.00	5.40	100.00	5.40	100.00
Co	3.00	5.20	96.29	5.40	100.00
Mn	3.00	5.20	98.15	5.29	98.29
Mg	2.95	5.20	96.29	5.20	96.29
Pb	2.93	5.40	100.00	5 00	92.50
Cd	3.30	5.40	100.00	4.40	90.74
Zn	3.60	5.40	100.00	5.00	92.50
Fe	3.06	5.20	96.29	5.20	96.29

Separation in succinate medium : These separations are based upon the processes of selective sorption and selective elution. Pb^{2+}, Cd^{2+}, Zn^{2+}, Mg^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+} and In^{3+} do not form anionic succinate complexes and therefore are not retained on the column when sorbed along with Bi(III) and hence can be separated by selective sorption. A 0.5-1% solution of succinic acid was used. Results are given in Table 4.

It was observed that Th^{4+} also forms a reasonably strong complex with succinic acid and is absorbed on the resin under the experimental conditions. However. it can be eluted before Bi(III) with 1N HNO_3 by selective elution.

Similar separations are possible using liquid anion-exchanger, Amberlite LA-I (Table 5). For a clear separation of layers 2 ml of 1% solution of NH_4Cl or $(NH_4)_2SO_4$ is added. A 0.5-1% solution of succinic acid and 10% Amberlite LA-1 in xylene are used.

Application to analysis of Wood's Metal : The sample of Wood's metal (0.02 g) is dissolved in a few drops of conc. HNO_3 and diluted to 10 ml. Added 20 ml of 2% maleic acid and *pH* is adjusted between 2 and 3. The mixture is sorbed on the column of anion-exchanger (2.5 g). After flushing the column with water, Bi(III) is eluted with 2N H_2SO_4 and determined as described earlier. Analysis is also carried out using the liquid anion-exchanger. The results are given in Table 6.

TABLE—6

ANALYSIS OF WOOD'S METAL

Method	Bi(III) found*	Reported value (BDH sample)
Amberlite IRA-401	48.60%	50%
Amberlite LA-1	49.30%	

* Average of two experiments

Thus, the method is quite useful and convenient for the separation of Bi(III) from other related metals. The added advantage is that both maleic acid and succinic acid do not interfere in the complexometric titrations with EDTA. The method is recommended for the determination of Bi(III) in alloys.

Acknowledgement

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N-Hydroxy-N-p-Chlorophenyl-N′-(2,5-Dimethyl) Phenyl-p-Toluamidine Hydrochloride as an Analytical Reagent for Gravimetric Determination of Copper**

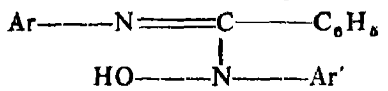
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N-Hydroxy-N-p-Chlorophenyl-N′-(2, 5-dimethyl) phenyl-p-toluamidine hydrochloride is proposed as a new sensitive and highly selective reagent for the gravimetric determination of copper(II). The thermally stable and directly weighable buff coloured copper complex of the reagent having the composition Cu($C_{22}H_{20}N_2OCl)_2$ gets quantitatively precipitated in the pH range 3.7-11.0. Many foreign ions including Fe^{3+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Cd^{2+}, MoO_4^{2-} and WO_4^{2-} can coexist during the determination without any adverse effect. The infrared spectral studies of the reagent and the copper complex has been made. The method has been applied to various copper alloys.

RECENT communications from this laboratory have shown that N-hydroxy-N,N′-diarylbenzamidiness, I, possessing a new type of function



I

$-N(OH)-\overset{|}{C}=N-$ are valuable reagents for carrying out gravimetric[1-3] and spectrophotometric[4-7] determination of a large number of transition metal ions. In connection with our studies on synthesis and analytical applications of N,N′-disubstituted hydroxyamidines, this paper reports the newly synthesised reagent, N-hydroxy-N-p-chlorophenyl-N′-(2,5-dimethyl)phenyl-p-toluamidine hydrochloride as a highly selective reagent for gravimetric determination of copper(II). The proposed reagent quantitatively precipitates buff coloured copper complex in the pH range 3.7-11.0. The complex possessing a small copper content (8.034%) can be safely dried at 110-170° within 30 min and directly weighed as Cu($C_{22}H_{20}N_2OCl)_2$. The proposed method offers the advantages of simplicity, rapidity and selectivity. So far as sensitivity and selectivity are concerned, the present method can be favourably compared with all the established methods[8-17].

Experimental

Apparatus : The infrared spectra of the reagent and its copper complex were recorded as mulls in hexachlorobutadiene (3700-2000 cm^{-1} and 1500-1300 cm^{-1}) and nujol (2000-1500 cm^{-1} and 1300-600 cm^{-1}) on a Perkin-Elmer 221 spectrophotometer equipped with sodium chloride optics. The *p*H of the solutions were adjusted with dilute acetic acid, ammonium acetate and dilute ammonia and measured with a Systronic *p*H meter Type 322.

*Reagennt : N-Hydroxy-N-*p*-chlorophenyl-N′-(2,5-dimethyl) Phenyl-*p*-toluamidine Hydrochloride :* The reagent was prepared by condensing equimolar quantities of N-(2,5-dimethyl) phenyl-p-toluimidoyl chloride and N-p-chlorophenylhydroxylamine in ether at 0-5° following the method of Deb and Mishra[18]. The resulting white crystals of the ligand were crystallised from minimum volume of absolute alcohol containing a few drops of concentrated hydrochloric acid (B.D.H.A.R.). White shining crystals of the compound melted at 166°. Yield ; 65%. (Found : C, 66.20 ; H, 5.68 ; N, 6.79%. Calcd. for $C_{22}H_{22}N_2OCl_2$: C, 65.83 ; H, 5.48 ; N, 6.98%). A 1% solution of the reagent in 90% ethyl alcohol was used for precipitation purposes.

Copper(II) solution : A stock solution of copper(II) was prepared by dissolving copper metal (B.D.H., AnalaR) in dilute nitric acid and the solution boiled to expel oxides of nitrogen. The metal content of this solution was determined gravimetrically employing salicylaldoxime[19].

All the chemicals used were of A.R. or G.R. grade.

Procedure : A suitable aliquot of the solution containing 2-25 mg of copper(II) was diluted to 125 ml with distilled water in a 400 ml beaker. The *p*H of the solution was adjusted between 3.7-11.0 with acetic acid, ammonium acetate or ammonia and the solution was heated to 50-60°. To this, was

** Presented at Annual Convention of Chemists—1977 held at Jaipur.

* Senior Author.

added the reagent solution (3 ml of 1% reagent solution per 2 mg of copper) with constant stirring till complete precipitation. The precipitated buff coloured copper complex was digested for about 20 min over a boiling water bath. The solution, while still hot was filtered through a preweighed G-3 sintered crucible. The complex was washed with hot water followed by hot 30% ethanol till the washings gave no colour with ferric chloride. The copper complex was dried at 110-120° to constant weight and weighed as $Cu(C_{22}H_{20}N_2OCl)_2$. Gravimetric factor is 0.08034. The results of these determinations are summarised in Table 1.

TABLE—1 DETERMINATION OF COPPER(II)

pH, 3.9±0.1

Copper taken (mg)	Weight of copper complex (mg)	Copper found (mg)	Rel. error %
1.20	14.8	1.19	−0.83
2.40	29.8	2.39	−0.41
5.00	69.1	4.99	−0.20
12.00	149.4	12.00	Nil
20.00	249.1	20.01	+0.05
25.00	311.6	25.03	+0.12

Results and Discussion

Properties and composition of the complex : The buff coloured copper complex is insoluble in water, ethanol and methanol and slightly soluble in chloroform, carbon tetrachloride and dioxane. The results of copper and nitrogen analysis suggest the composition of the chelate to be $Cu(C_{22}H_{20}N_2OCl)_2$ (Found : Cu, 8.03 ; N, 7.01% Calcd. Cu, 8.03 ; N, 7.08%). The examination of the infrared spectra of the ligand revealed three strong bands at 2450 $(=\overset{+}{N}-H)$, 1610$(C=\overset{+}{N})$ and 950 $cm^{-1}(N-O)$. The band due to $=\overset{+}{N}-H$ stretching is absent in the spectra of the copper complex. This suggests the deprotonation of the charged azomethine nitrogen atom during complex formation. Thus, the liberated free base produces copper(II) complex probably by forming a Cu–O bond (through the hydroxyloxygen) and coordination takes place through the formation of a Cu–N=C type of bond. This view, that the azomethine nitrogen atom provides the coordination site is also favoured by the fact that the $C=\overset{+}{N}$ frequency of the ligand is lowered in the complex (1570 cm^{-1}). The formation of Cu–O–N is also evident from the displacement of N–O stretching frequency of the ligand to 960 cm^{-1} in the complex.

Effect of pH and amount of reagent : The precipitation of the copper complex commenced at pH 2.2 and was quantitative between pH values of 3.7–11.0. A slight excess of the reagent to exceed 1 : 2 metal to reagent ratio was found to be sufficient for complete precipitation of the metal complex. A large excess of the reagent showed no adverse effect on the determination and can be washed out very easily with ethanol in which the complex is practically insoluble. Thus, an excess of 900 mg of the reagent in a final volume of 150 ml was found to have no interfering effect on the determination of 12.00 mg of copper.

Effect of masking agents : High concentrations of masking agents such as thiourea, triethanolamine, citric acid, tartaric acid and fluoride caused no harm to the precipitation and determination of copper. However, in presence of excess EDTA copper was completely masked.

Influence of foreign ions : A known amount of cation or anion was mixed with a fixed amount of copper (12.00 mg) and the determination was carried out at pH 3.7-6.0 as outlined in the general procedure. Alkali metals, alkaline earths, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Al^{3+}, Cr^{3+}, UO_2^{2+}, Te^{4+}, Se^{4+} and Th^{4+} did not interfere with the estimation of copper. The ions such as Fe^{3+}, Bi^{3+}, Sb^{3+}, Ti^{4+} and VO_3^- were effectively masked with tartaric acid (3.0 g). In the presence of MoO_4^{2-} and WO_4^{2-}, the alcoholic concentration of the precipitation media was maintained at 50-60% by volume and the copper complex was washed with ethanol for several times. The partial hydrolysis of Sn^{4+} and Zr^{4+} was prevented by adding NaF or KF (2.5 g) and that of Ce^{4+} by ammonium sulphate (2 g). La^{3+} was tied up with ammonium acetate (2.5 g). Among anions, chloride, bromide, fluoride, borate, sulphate, acetate, oxalate, nitrate, arsenate and phosphate had no interfering effect on the determination. The results of the determinations are shown in Table 2.

TABLE—2 DETERMINATION OF COPPER IN PRESENCE OF FOREIGN IONS

(Copper taken = 12.00 mg ; pH, 3.9±0.1)

Diverse ions added (mg)	Weight of complex obtained (mg)	Copper found (mg)	Error % (mg)
Fe^{3+}(60)	149.2	11.98	−0.16
Al^{3+}(60)	149.6	12.2	+0.16
Cr^{3+}(60)	149.4	12.02	Nil
Bi^{3+}(50)*	149.3	11.99	−0.08
Sb^{3+}(40)*	149.5	12.01	+0.08
Ni^{2+}(50)	149.5	12.01	+0.08
Co^{2+}(50)	149.3	11.99	+0.08
Mn^{2+}(50)	149.5	12.01	−0.25
Hg^{2+}(60)	149.1	11.97	+0.08
La^{3+}(40)	149.8	12.03	+0.25
Ti^{4+}(25)*	149.3	11.99	−0.08
Zr^{4+}(40)(a)	149.3	11.99	−0.08
Tn^{4+}(50)	149.2	11.98	−0.16
UO_2^{2+}(40)	149.5	12.01	+0.08
VO_3^-(30)*	149.5	12.01	+0.08
MoO_4^{2-}(75)	149.6	12.02	+0.16
WO_4^{2-}(50)	149.2	11.98	−0.16

* In presence of 3 g of tartaric acid in 125 ml of the solution

(a) In presence of 2.5 g of NaF.

Standard deviation : The relative standard deviation of the method for the determination of 12.00 mg of copper was ± 0.12% (x = 30).

Determination of copper in alloys: To test the validity of the method three standard alloys obtained from Bureau of Analysed Samples, Ltd., Middlesbrough, Yorks, England were analysed for copper using the present reagent. The results summarised in Table 3 indicates that the proposed method gives precise and accurate results,

TABLE—3 DETERMINATION OF COPPER IN ALLOYS

Sample No. and name	Copper found[a] %	Certified value %	Standard deviation
8 c White metal	4.08	4.10	±0.014
5 f Brass	70.75	70.8	±0.060
6 f Gun metal	87.84	87.9	+0.074

a=average of 4 determinations

An accurately weighed amount of the alloy selected to provide 10-15 mg of copper in a 25 ml aliquot of the final solution was dissolved in 40% nitric acid. The solution was evaporated to a small volume and after dilution to 100 ml with water, precipitated tin and antimony oxides were filtered off. The precipitate was thoroughly washed with dilute nitric acid. The filtrate was again evaporated to near dryness and diluted with water. The solution was transferred to a 250 ml volumetric flask and diluted to volume. A 25 ml aliquot of the solution was pipetted in a 400 ml beaker and 1 g of tartaric acid was added. The amount of copper was determined following the recommended procedure.

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Synthesis of Some New 5-Mercapto 3-Substituted Quinazolone-s-Triazoles ; Their Reaction with Dibromo Alkanes

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5-Mercapto 3-substituted quinazolone-s-triazoles(VII) obtained by the cyclisation of corresponding quinazolone thiosemicarbazides(VI) were reacted with 1,2-dibromoethane and 1,3-dibromopropane to yield 2-substituted 5, 6-dihydrothiazolo[3, 2-b]-s-triazoles(VIII) and 2-substituted 5H-6, 7-dihydro-s-triazolo[3, 2-b] [1, 3]-thiazines(IX) respectively. These compounds were also screened for their antifungal activity against *Alternaria alternata*, *Drechslera papendorfii* and *Helminthosporium oryzae*. Only quinazolone thiosemicarbazides(VI) showed measurable activity.

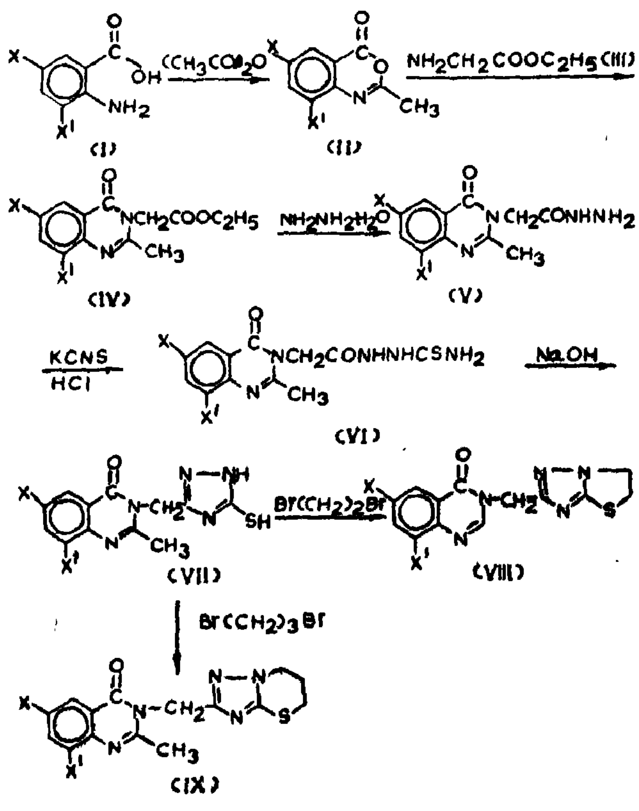
CONTINUED interest in incorporating a quinazolone nucleus, capable of exhibiting hypnotic[1], anticonvulsant[2], analgesic[3], antifungal and antibacterial[4] properties led Devani *et al* to synthesise some 2,3,4-trisubstituted quinazolone sulphonyl thioureas[5]. These were tested for their antibacterial activity. Some 2-amino-4(3H)-quinazolones have also been reported to possess fungicidal activity[6]. On the other hand, various thiosemicarbazides[7] and their cyclised products, oxadiazoles and *s*-triazoles[8] have been reported to possess antibacterial and antifungal activity. Recently some thiazolo[3,2-b]-*s*-triazoles and *s*-triazolo[3,2-b][1,3]-thiazines have been synthesised and evaluated for their fungicidal activity[9].

These findings prompted us to synthesise some new quinazolones by incorporating a heterocyclic ring at position 3 of quinazolone nucleus with a view to study their antifungal activity. Accordingly 5-mercapto 3-substituted quinazolone-*s*-triazoles (VII) were obtained by refluxing corresponding thiosemicarbazides(VI) with 8% sodium hydroxide solution. The reaction of 1,2-dibromoethane with (VII) in anhydrous ethanol gave 2-quinazolone 5,6-dihydrothiazolo[3,2-b]-*s*-triazoles(VIII).

The structure of compounds (VIII) has been supported by their correct analytical data (Table 3). The IR spectra of compounds (VIII) showed characteristic absorption bands at 1675-1668 cm^{-1} (endocyclic C=O), 1600-1590 cm^{-1}(C=N), 1505-1440 cm^{-1} (C−N stretching), 1365-1320 cm^{-1} (C−S−C) and 2955-2900 cm^{-1} (C−CH_3).

Similarly when compounds (VII) were refluxed with 1,3-dibromo-propane in anhydrous ethanol furnished 2-substituted quinazolone 5H-6,7-dihydro-*s*-triazolo[3,2-b][1,3]-thiazines(IX).

The structure of compounds (IX) has been supported by their correct analytical data (Table 4) and IR spectra showed absorption bands at 1677-1665 cm^{-1} (endocyclic C=O), 1595-1585 cm^{-1} (C=N). 1510-1450 cm^{-1}(C−N stretching), 1390-1350 cm^{-1} (C−S−C) and 2950-2920 cm^{-1} (C−CH_3).



Experimental

All melting points were taken in open capillary tubes and are uncorrected. The IR absorption spectra were determined in KBr pallets on Perkin-Elmer infrared spectrophotometer.

Substituted anthranilic acids(I)[10-12], acetanthranil(II)[13], ethyl glycine ester(III)[14], quinazolone esters(IV)[15], and quinazolone hydrazides(V)[15] were prepared by following the known methods.

Quinazolone thiosemicarbazides(VI)

A mixture of appropriate quinazolone hydrazide (V) (0.01 mole), potassium thiocyanate (0.01 mole), concentrated HCl (0.8 ml) and water (20 ml) was refluxed for 4 hrs. The reaction mixture was cooled to obtain the corresponding quinazolone thiosemicarbazide, which was filtered, washed with water and crystallised from suitable solvents. The results are recorded in Table 1. The IR spectrum of 2-methyl-3-acetyl thiosemicarbazide-4-quinazolone showed characteristic absorption bands at 1690 cm^{-1} (endocyclic C=O), 1658 cm^{-1} (CONH), 1600 cm^{-1} (C=N). 1470 cm^{-1}, 1445 cm^{-1} and 1390 cm^{-1} (C–N stretching). 1240 cm^{-1} (C=S), 3380 cm^{-1} and 3200 cm^{-1} (N–H stretching) and 2910 cm^{-1} ($\overset{|}{C}-CH_3$)

TABLE—1. QUINAZOLONE THIOSEMICARBAZIDES(VI)

Sl. No.	X	X′	Yield %	M.P. °C	Molecular Formula	Found / Calcd. %N	%S
1.**	H	H	50	290	$C_{12}H_{13}N_5O_2S$	23.87 24.06	10.02 10.99
2.*	H	Br	47	245	$C_{12}H_{12}BrN_5O_2S$	18.24 18.92	8.04 8.65
3.**	Br	Br	52	304	$C_{12}H_{11}Br_2N_5O_2S$	14.93 15.59	6.75 7.13
4.*	H	I	42	249	$C_{12}H_{12}IN_5O_2S$	15.89 16.79	6.97 7.67
5.**	Cl	Cl	44	316	$C_{12}H_{11}Cl_2N_5O_2S$	19.28 19.44	8.85 8.89

* Crystallised from ethanol, ** Crystallised from acetic acid

5-Mercapto 3-substituted quinazolone-s-triazoles (VII)

Appropriate quinazolone thiosemicarbazide(VI) (0.01 mole) in 8% sodium hydroxide solution was refluxed for about 3 hrs. The reaction mixture was cooled and acidified with dilute acetic acid. The precipitate thus obtained was filtered, washed with water, dried and crystallised from ethanol. The results are recorded in Table 2. The IR spectrum of 5-mercapto 3-(6′,8′-dibromo quinazolone)-*s*-triazole showed absorption bands at 1690 cm^{-1} (endocyclic C=O), 1590 cm^{-1}(C=N), 1480 cm^{-1}, 1445 cm^{-1} and 1420 cm^{-1} (C–N stretching), 3470 cm^{-1} and 3360 cm^{-1} (N–H stretching), 740 cm^{-1} (C–S) and 2910 cm^{-1} (S–H and $\overset{|}{C}-CH_3$).

TABLE—2. 5-MERCAPTO 3-SUBSTITUTED QUINAZOLONE-*s*-TRIAZOLES(VII)

Sl. No.	X	X′	Yield %	M.P. °C	Molecular Formula	Found / Calcd. %N	%S
6.	H	H	47	310	$C_{12}H_{11}N_5OS$	25.12 25.64	11.39 11.72
7.	H	Br	43	199	$C_{12}H_{10}BrN_5OS$	19.32 19.89	8.67 9.09
8.	Br	Br	55	241	$C_{12}H_9Br_2N_5OS$	15.89 16.24	6.94 7.42
9.	H	I	45	189	$C_{12}H_{10}IN_5OS$	16.98 17.54	7.58 8.02
10.	Cl	Cl	48	289	$C_{12}H_9Cl_2N_5OS$	19.04 20.47	9.69 9.36

2-Substituted quinazolone 5,6-dihydrothiazolo [3,2-b]-s-triazoles(VIII)

A mixture of appropriate 5-mercapto 3-substituted quinazolone-*s*-triazole(VII) (0.01 mole) 1,2-dibromoethane (0.01 mole) in anhydrous ethanol (60 ml) was refluxed on steam bath for 36-40 hrs. The cooled reaction mixture was neutralised with ammonium hydroxide. The product that separated out was filtered, washed with water and crystallised from ethanol. The results are recorded in Table 3.

TABLE—3. 2-SUBSTITUTED QUINAZOLONE 5, 6-DIHYDROTHIAZOLO 3, 2-b-*s*-TRIAZOLES(VIII)

Sl. No.	X	X′	Yield %	M.P. °C	Molecular Formula	Found / Calcd. %N	%S
11.	H	H	38	249	$C_{14}H_{13}N_5OS$	22.90 23.41	9.20 10.70
12.	H	Br	32	117	$C_{14}H_{12}BrN_5OS$	18.18 18.52	7.56 8.40
13.	Br	Br	44	211	$C_{14}H_{11}Br_2N_5OS$	14.86 15.32	6.92 7.00
14.	H	I	39	238	$C_{14}H_{12}IN_5OS$	16.32 16.47	7.19 7.33
15.	Cl	Cl	41	259	$C_{14}H_{11}Cl_2N_5OS$	18.57 19.02	7.92 8.69

2-Substituted quinazolone 5H-6,7-dihydro-s-triazolo-[3,2-b] [1,3]-thiaxines(IX)

A mixture of appropriate 5-mercapto 3-substituted quinazolone-*s*-triazole(VII) (0.01 mole) and 1,3-dibromopropane (0.01 mole) was refluxed in anhydrous ethanol (60 ml) for about 40 hrs. The cooled reaction mixture was neutralised with ammonium hydroxide. The product that separated out was filtered, washed with water and crystallised from ethanol. The results are recorded in Table 4.

Antifungal activity

All the compounds synthesised were screened for their antifungal activity against *Alternaria alternata, Drechslera papendorfii* and *Helminthosporium oryzae* at concentrations 2%, 0.2%, 0.02% and 0,002% (W/V) by Paper-disc plate method[14]. Only quinazolone

TABLE—4. 2-SUBSTITUTED QUINAZOLONE 5H-6, 7-DIHYDRO-s-TRIAZOLO[3, 2.b][1, 3]-THIAZINES(IX)

Sl. No.	X	X'	Yield %	M.P. °C	Molecular Formula	Found / Calcd. %N	%S
16.	H	H	41	172	$C_{15}H_{15}N_5OS$	22.02 22.36	9.92 10.22
17.	H	Br	34	278	$C_{15}H_{14}BrN_5OS$	16.58 17.86	7.56 8.16
18.	Br	Br	47	262	$C_{15}H_{13}Br_2N_5OS$	14.29 14.86	5.89 6.79
19.	H	I	36	263	$C_{15}H_{14}IN_5OS$	14.98 15.95	6.94 2.29
20.	Cl	Cl	39	221	$C_{15}H_{13}Cl_2N_5OS$	17.88 18.32	7.95 8.38

thiosemicarbazides(VI) listed in Table 1 were found to possess measurable antifungal activity against all the three fungi at concentration 2%, while the compounds listed in Tables 2, 3 and 4 were completely devoid of antifungal activity.

Acknowledgement

The authors are thankful to Dr. D. R. Gupta, Head of the Department of Chemistry, G. B. Pant University of Agriculture and Technology, Pantnagar, Dr. D. S. Bhakuni, C.D.R.I., Lucknow and Dr. H. D. Pathak, Head of the Department of Chemistry, D. S. B. College, Nainital for encouragement and useful suggestions.

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Studies in the Synthesis of Furochromones : Part—IV

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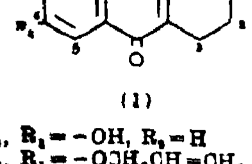
Manuscript received 2 November 1977, revised 15 March 1978, accepted 3 April 1978

Thermal condensation of 2-methylresorcinol with ethyl cyclopentanone-2-carboxylate gave 7-hydroxy-8-methyl-1, 2, 3, 4-tetrahydrocyclopenta(b)benzopyran-4-one(Ia), which on allylation followed by Claisen rearrangement gave 6-allyl-7-hydroxy-8-methyl-1, 2, 3, 4-tetrahydrocyclopenta(b)benzopyran-4-one(Ic). (Ic) was converted to 9-methyl-1, 2, 3, 4-tetrahydrocyclopenta(b)furo(3,2-*g*)benzopyran-4-one(IIa) by treatment with osmium tetroxide followed by polyphosphoric acid. (IIb) was obtained by treating (Ic) with conc. sulphuric acid followed by dehydrogenation with palladised charcoal(10%).

In recent years furochromones have received considerable attention as they not only occur in nature but also possess therapeutic properties. It was, therefore, thought of interest to synthesise Khellin[1] and Visnagin[2] type of compounds which are likely to be physiologically active.

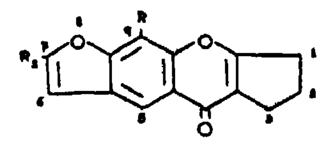
In continuation of our work on the synthesis of furochromones[3], we report here the synthesis of 9-methyl-1,2,3,4-tetrahydrocyclopenta(b)furo(3,2-*g*)-benzopyran-4-one(II*a*),7,9-dimethyl-1,2,3,4-tetrahydrocyclopenta(b)furo(3,2-*g*)-benzopyran-4-one(II*b*). Condensation of 2-methylresorcinol with ethyl cyclopentanone-2-carboxylate in refluxing diphenyl ether according to Desai, Trivedi and Sethna[4] gave 7-hydroxy-8-methyl-1,2,3,4-tetrahydrocyclopenta(b)-benzopyran-4-one(I*a*). This on allylation with allyl bromide afforded the corresponding 7-allyl ether derivative(I*b*) which was subjected to Claisen rearrangement to give 6-allyl-7-hydroxy-8-methyl-1, 2,3,4-tetrahydrocyclopenta(b)benzopyran-4-one(I*c*). (I*c*) on treatment with osmium tetroxide and potassium periodate[5] in ethyl acetate. afforded 7-hydroxy-8-methyl-6-acetaldehydo-1,2,3,4-tetrahydrocyclopenta(b)benzopyran-4-one(I*d*). Cyclisation of (I*d*) with polyphosphoric acid gave 9-methyl-1,2, 3,4-tetrahydrocyclopenta(b)furo(3,2-*g*)benzopyran-4-one(II*a*).

Cyclisation of (I*c*) by trituration with conc. sulphuric acid according to Shaikh and Trivedi[6] afforded 7,9-dimethyl-1,2,3,4,6,7-hexahydrocyclo-



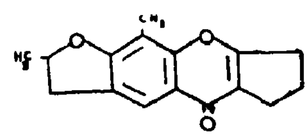
(I)

(I*a*) $R = -CH_3$, $R_1 = -OH$, $R_2 = H$
(I*b*) $R = -CH_3$, $R_1 = -OCH_2CH=CH_2$, $R_2 = H$
(I*c*) $R = -CH_3$, $R_1 = -OH$, $R_2 = -CH_2CH=CH_2$
(I*d*) $R = -CH_3$, $R_1 = -OH$, $R_2 = -CH_2CHO$



(II)

(II*a*) $R = -CH_3$, $R_1 = H$
(II*b*) $R = R_1 = -CH_3$,



(III)

penta(b)furo(3, 2-*g*)-benzopyran-4-one(III). Dehydrogenation of (III) with palladised charcoal in boiling diphenyl ether furnished 7.9-dimethyl-1,2,3, 4-tetrahydrocyclopenta(b)furo(3, 2-*g*)benzopyran-4-one(II*b*).

Experimental

7-Hydroxy-8-methyl-1,2,3,4-tetrahydrocyclopenta(b)-benzopyran-4-one(Ia) :

A mixture of 2-methylresorcinol (3 g) and ethyl cyclopentanone-2-carboxylate (4 ml) was refluxed with diphenylether (10 ml) for three hours with a short condenser to facilitate the removal of alcohol formed. After cooling the separated p roduct was filtered and washed several times with petroleum ether. It crystallised from dimethyl formamide. m.p. 309°, yield 2 g. (Found : C, 71.54 ; H, 5.47 ; $C_{13}H_{12}O_3$ requires C, 72.21 ; H, 5.55%).

7-Allyloxy-8-methyl-1,2,3,4-tetrahydrocyclopenta(b)-benzopyran-4-one(Ib) :

A mixture of 7-hydroxy-8-methyl-1,2,3,4-tetrahydrocyclopenta(b)benzopyran-4-one (2 g) allyl bromide

(1.2 g) and anhydrous potassium carbonate (5 g) was refluxed in dry dimethyl formamide (150 ml) in a water bath for 10 hrs. The reaction mixture was poured into water. The separated product was filtered and washed with very dilute sodium hydroxide solution to remove unreacted compound and crystallised from alcohol. m.p. 137°, yield 1.3 g. (Found : C, 74.86 ; H, 5.95 ; $C_{16}H_{16}O_3$ requires C, 75.00 ; H, 6.25%).

6-Allyl-7-hydroxy-8-methyl-1,2,3,4-tetrahydrocyclopenta(b)benzopyran-4-one(Ic) :

7-Allyloxy-8-methyl-1,2,3,4-tetrahydrocyclopenta-(b)benzopyran-4-one (2 g) was refluxed with dimethylaniline (10 ml) for 8 hrs., after cooling the reaction mixture was poured into conc. hydrochloric acid (50 ml) containing pieces of ice. The separated product was filtered and dissolved in sodium hydroxide solution. The solution was filtered. The filterate on acidification with conc. hydrochloric acid gave the product which was filtered and crystallised from acetic acid, m.p. 222°, yield 1.5 g. (Found : C, 74.74 ; H, 6.28 ; $C_{16}H_{16}O_3$ requires C, 75.00 ; H, 6.25%). IR spectrum (nujol) 1635 cm^{-1} (γ-pyronyl>C=O group) and a broad band at 3300 cm^{-1} (aromatic hydroxy group).

6-Acetaldehydo-7-hydroxy-8-methyl-1,2,3,4-tetrahydrocyclopenta(b)benzopyran-4-one(Id) :

7-Hydroxy-6-allyl-8-methyl-1, 2, 3, 4-tetrahydrocyclopenta(b)benzopyran-4-one (500 mg) dissolved in ethyl acetate (100 ml) was vigorously shaken with osmium tetroxide (50 mg) and water (100 ml). To the dark solution was added potassium periodate (2 g in 0 ml water) dropwise over a period of 3 hrs. The ethyl acetate layer was separated, dried and evaporated. The residue was dissolved in chloroform and the clear solution was percolated through a short column of alumina. The residue left after evaporation of chloroform crystallised from alcohol, m.p. 260° (decomp.), yield 0.3 g. (Found : C, 69.76 ; H, 5.51 ; $C_{15}H_{14}O_4$ requires C, 69.69 ; H, 5.42%).

9-Methyl-1,2,3,4-tetrahydrocyclopenta(b)furo(3,2-g)-benzopyran-4-one(IIa) :

6-Acetaldehydo-7-hydroxy-8-methyl-1,2,3,4-tetrahydrocyclopenta(b)benzopyran-4-one (250 mg) was heated with polyphosphoric acid (10 ml) in a water bath for 1½ hr., and then poured into ice water. The solid separated was filtered and washed with dilute sodium hydroxide solution to remove uncyclised compound. A chloroform extract of the dried residue was passed over a short column of alumina. Evaporation of solvent left a product which crystallised from benzene, m.p. 266°, yield 100 mg. (Found : C, 74.84 ; H, 5.01 ; $C_{15}H_{12}O_3$ requires C, 75.00 ; H, 5.00%). IR spectrum (nujol) 875 cm^{-1} (furan ring), 1615 cm^{-1} (γ-pyronyl>C=O group). $\lambda_{max}^{chloroform}$ 246 nm (log *e* 4.76), 278 nm (log *e* 4.17), 314 nm (log *e* 3.99).

7,9-Dimethyl-1, 2, 3, 4, 6,7-hexahydrocyclopenta(b)-furo(3,2-g)benzopyran-4-one(III) :

6-Allyl-7-hydroxy-8-methyl-1, 2, 3, 4-tetrahydrocyclopenta(b)benzopyran-4-one(1 g) was triturated with conc. sulphuric acid (5 ml) in a water bath for 10 min. The content were poured into crushed ice. The separated product was filtered and washed with dilute sodium hydroxide solution to remove uncyclised compound. It crystallised from benzene, m.p. 154°, yield 0.8 g. (Found : C, 75.01 ; H, 6.45 ; $C_{16}H_{16}O_3$ requires C, 75.00 ; H, 6.25%). IR spectrum (nujol) 1630 cm^{-1} (γ-pyronyl>C=O group). $\lambda_{max}^{methanol}$ 249 nm (log *e* 4.18) 300 nm (log e 4.18).

7,9-Dimethyl-1,2,3,4-tetrahydrocyclopenta(b)furo(3, 2-g)benzopyran-4-one(IIb) :

A mixture of 7,9-dimethyl-1,2,3,4,6,7-hexahydrocyclopenta(b)furo(3,2-*g*)benzopyran-4-one(0.5 g) and palladised charcoal (10% ; 0.3 g) and diphenyl ether (4 ml) was refluxed for 10 hrs. The reaction mixture was filtered hot and petroleum ether was added to the cooled filterate. The separated product was filtered and washed several times with petroleum ether. The product was purified by passing its benzene solution over a short column of alumina. Evaporation of solvent left a product which crystallised from benzene, m.p. 212°, yield 0.2. g. (Found : C, 76.17 ; H, 5.53 ; $C_{16}H_{14}O_3$ requires C, 76.00 ; H, 5.51%). IR spectrum (nujol) 835 cm^{-1} (furan ring), 1630 cm^{-1} (γ-pyronyl>C=O group). $\lambda_{max}^{methanol}$ 246 nm (log *e* 4.82), 290 nm (log *e* 4.19), 298 nm (log *e* 4.11), 320 nm (log *e* 4.03).

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Heterocyclic Quinones : Part I—Synthesis of Benzo(1:2-b, 4:5-b′) dibenz(f,f′)-Pyrrocoline Quinones

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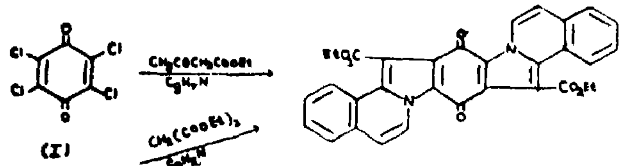
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Manuscript received 31 March 1977, revised 5 November 1977, accepted 24 February 1978

A series of unsymmetrical disubstituted benzo(1 : 2-b), 4 : 5-b′)-dibenz(f, f′)-pyrrocoline quinones has been synthesised by condensing chloranil with active methylene compounds and isoquinoline which gave only the trans form of the compound as shown by colour reaction and T.L.C. The deep colour of these compounds is attributed to the betaine structure as one of the contributing form.

TILAK and VENKITESWARAN[1,2] have reported a method for the preparation of pyrrocoline quinones from chloranil and 2 : 3 dichloro-1 : 4 naphthoquinone. Several compounds containing a reactive methylene group were reacted with chloranil and pyridine and in each case a pair of corresponding 5,11-disubstituted benzo(1 : 2-b, 4 : 5-b′)-dipyrrocoline-6 : 12-quinone and 5,7-disubstituted-benzo(1 : 2-b, 4 : 5-b′)-dipyrrocoline-6 : 12-quinone as geometrical isomers was obtained[2], Considering the evidences[2,3,4] leading to the above structures, it seemed interesting to carry out the reaction of chloranil and reactive methylene compounds with isoquinoline, with the hope of obtaining benzo(1 : 2-b. 4 : 5-b′)-dibenz(f. f′) pyrrocoline 8,16-quinones.

Interaction of chloranil. acetoacetic ester and isoquinoline gave compound (A), m.p. 328-30°. It gave a brilliant blue colour in conc. H_2SO_4 which turned red with precipitation on basification and the blue colour reappeared on addition of conc. H_2SO_4. This indicates that only the transform is obtained and is actually 7,15 dicarbethoxy-benzo-(1 : 2-b, 4 : 5-b′)-dibenz(f, f′)-pyrrocoline-8 : 16-quinone. The compound gives beautiful pink colour with fluorescence in benzene.

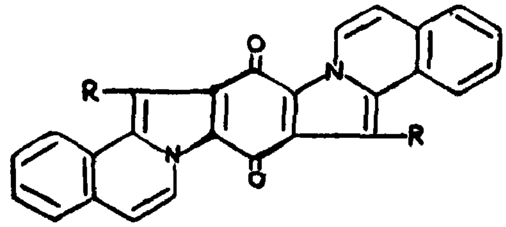


(A)

Similarly with malonic ester, the same compound (A) is obtained. m.p. 327-29° confirmed through TLC.

Interaction of I with acetyl acetone and benzoyl acetone in presence of isoquinoline gave compounds (B) and (C) respectively. Their structures have been established by colour reactions (as in the case of (A)) as 7 : 15-diacetyl-benzo(1 : 2-b, 4 : 5-b′)-dibenz(f, f′)-pyrrocoline-8 : 16-quinone and 7 : 15-dibenzoyl-benzo(1 : 2-b, 4 : 5-b′)-dibenz(f, f′)-pyrrocoline-8 : 16-quinone respectively.

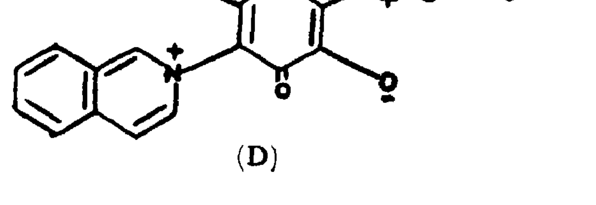
$$I + CH_3COCH_2R \xrightarrow{C_9H_7N}$$



(B) $R = COCH_3$
(C) $R = COC_6H_5$

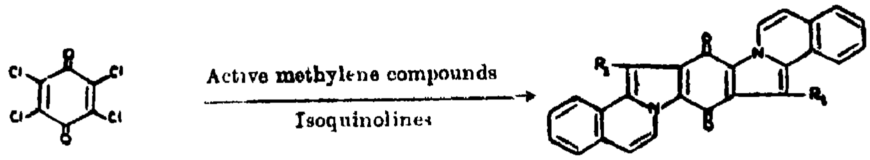
The colour reactions of the said compounds indicate that the products should have a trans-configuration, which is the only product isolated in this case. The formation of cis structure seems to be sterically hindered.

Interaction of I, methyl cyanide and isoquinoline gave a yellow coloured product, which could be extracted into chloroform giving a yellow coloured solution which was decolourized on acidification with dil. HCl. It however did not give the above colour reactions and was fouud to be the inner salt (the betaine)[5] represented by (D). The compound does not melt up to 356°, and was crystallized from glacial acetic acid.



(D)

TABLE—1. 7 : 15 DISUBSTITUTED-BENZO(1 : 2-b, 4 : 5-b')-DIBENZ(f, f') PYRROCOLINE-QUINONES



where, R_1 = $-COOEt$, $-COCH_3$, $-COC_6H_5$

Sl. No.	Active methylene compound used	Molecular formula	Crystallized from	Colour	M.P. 0°C	Found C %	Found H %	Found N %	Required C %	Required H %	Required N %
1.	Ethyl acetoacetate	$C_{32}H_{22}M_2O_6$	Benzene	Red	328-30	72.4	4.0	5.1	72.4	4.1	5.2
2.	Malonic ester	$C_{32}H_{22}N_2O_6$	Benzene	Brown-red	327-29	72.3	4.1	5.2	72.4	4.1	5.2
3.	Acetyl acetone	$C_{30}H_{18}N_2O_4$	Pyridine	Brown	does not melt up to 356	76.5	3.7	5.9	76.5	3.8	5.9
4.	Benzoyl acetone	$C_{40}H_{22}N_2O_4$	Pyridine	Dark-red	does not melt up to 356	80.7	3.6	4.5	80.8	3.6	4.6

Experimental Procedure

All melting points have been determined on a Kofler instrument and are uncorrected. General procedure adopted for the preparation of the benzo-(1 : 2-b, 4 : 5-b')-dibenz(f,f')-pyrrocoline quinone is as given below :—

A mixture of chloranil (0.1 mole) reactive methylene compound (0.1 mole) and isoquinoline (0.1 mole) in 25-30 ml absolute alcohol was heated under reflux on a water bath for 4 hrs., when all the chloranil dissolved and a deeply coloured reaction mixture was obtained. The product separated on cooling was filtered and washed with ethanol, ether, hot water and then dried. The product was recrystallized from the desired solvent.

All these quinones so prepared were mostly soluble in benzene, dioxane, pyridine and less soluble in acetone and alcohol. They are insoluble in water. They gave blue to violet coloured solution in concentrated sulphuric acid which turned red on basification followed by precipitation. They also give a beautiful pink to pink red colour in benzene showing fluorescence. Analysis of the various benzo-(1 : 2-b, 4 : 5-b')-dibenz(f, f')-pyrrocoline-quinones prepared are described in Table 1.

Mechanism

The reaction mechanism for the formation of 7 : 15 disubstituted benzo(1 : 2-b, 4 : 5-b')-dibenz-(f,f')-pyrrocoline quinones is based on a similar study[6] done on the reaction of active methylene compounds with 2 : 3 dichloro 1 : 4 naphthoquinone and corroborates the process of cleavage of the more electron withdrawing group R during the final stage of cyclisation.

Dyeing Properties :

The dyeing characteristics of these compounds is under investigation.

Acknowledgement :

Thanks are due to Prof. R. C. Kapoor, Head of Chemistry Department for providing necessary laboratory facilities and to the U.G.C., New Delhi, for the award of a Junior Research Fellowship to R. P. S.

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Synthesis of 8-Substituted-10,11-Dihydro-11-Oxo-5H-Dibenzo [b, e]-1,4-Diazepines

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8-Amino-10,11-dihydro-11-oxo-5*H*-dibenzo[*b*, *e*]-1, 4-diazepine (2) synthesised by the cyclisation of 2′, 4′-diaminodiphenylamine-2-carboxylic acid (1), was converted to its chloro- and iodo derivatives (3 and 4) by Sandmeyer reaction, and to bromo derivative (5) by Gattermann reaction.

DIBENZODIAZEPINES are used as antihistaminic, antiparkinson and neuroleptic drugs[1,2]. Tarpan[3], noveril[4] and clozapine[5] are some marketed drugs of this class. Dibenzodiazepines having substituent (as chlorine) at position-7 showed good pharmacological activity[6]. In order to find out pharmacological activity or otherwise of dibenzodiazepines with substituents at position other than position-7, we synthesised analogous compounds having halogen substituents at position-8 starting from the corresponding 8-amino-10,11-dihydro-11-oxo-5*H*-dibenzo [*b*,*e*]-1,4-diazepine (2)[7].

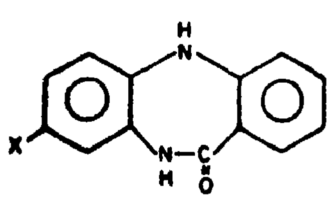
2,4-Dinitrochlorobenzene was reacted with anthranilic acid (Ullmann reaction) to give 2',4'-dinitro-diphenylamine-2-carboxylic acid (Ia)[6,7] which was reduced with sodium dithionite to give 2',4'-diaminodiphenylamine-2-carboxylic acid (c.a. 61%), and the latter was cyclised to 8-amino-10, 11-dihydro-11-oxo-5*H*-dibenzo [*b*,*e*]-1,4-diazepine (2). The amino group of the diazepine (2) was replaced by chlorine[8], iodine[9] and bromine[10] to afford the halogenodiazepines (3-5).

Experimental

All the melting points are uncorrected. Nmr spectra were recorded in DMSO on a varian-A-6OD model using TMS as internal reference. The purity of the compounds was ascertained by tlc using silica gel-G as stationary phase and C_6H_6 : C_2H_5OH : NH_3 (7 : 2 : 1, solvent layer) as mobile phase.

8-Chloro-10,11-dihydro-11-oxo-5H-dibenzo [b,e]-1,4-diazepine (3)

The diazotised solution of the compound (2) (1.1250 g, 0.005M in 3 ml of conc. HCl, 2 ml CH_3COOH and 0.4 g of $NaNO_2$ at 0-5) was added to a cold solution of Cu_2Cl_2 (0.350 g dissolved in 1.50 ml of conc. HCl and 3 ml of water) at 0° with continuous stirring. After stirring at 20° for half an hour the reaction mixture was finally heated for 1 hr. over water bath when evolution of N_2 ceased. The contents were cooled and filtered. The crude product was crystallised from C_2H_5OH. to afford the *diazepine (3)* (0.782 g, 63.99%), m.p 165°, Rf 0.65, (Found C, 64.02 ; H, 3.52 ; N, 11.56 ; Cl, 14.30, Calc. for $C_{13}H_9ON_2Cl$, C, 63.82 ; H, 3.68 ; N, 11.45 ; Cl, 14.54%) δ(DMSO) : 6.15-6.50 (1H, bs, Ar – NH – Ar), 7.05-8.15 (7H.m. ArH) and 9.60 (1H, s, Ar – NH – Co –).



8-Iodo-10,11-dihydro-11-oxo-5H-dibenzo[b,e]-1,4-diazepine(4)

To a diazotised solution of the compound (2) (1.1250 g, 0.005M, in 3 ml of conc. HCl, 2 ml of CH_3COOH and 0.4 g $NaNO_2$ at 0-5°) ice cold solution of KI (1.0 g, 0.006M) was added in 15 min with stirring. The reaction mixture was warmed over water bath for one hour and the contents were exhaustively extracted with $CHCl_3$ after basification with aq. NaOH (10%). The $CHCl_3$ extract was washed with thiosulphate solution and solvent distilled off. The crude product was crystallised from C_2H_5OH to afford diazepine (*4*) (0.815 g, 42.51%, mp 140°, Rf 0.56 ; Found C, 46,64 : H. 2.76 ; N, 8.48 ; I, 38.42 ; Calc. for $C_{13}H_9ON_2I$, C, 46.43 ; H, 2.68 ; N, 8.34 ; I, 37.80%) δ(DMSO) 6.15-6.50 (1H, bs, Ar – NH – Ar), 7.05-8.15 (7H, m, ArH) and 9.60 (1H, s, Ar – NH – Co –).

8-Bromo-10,11-dihydro-11-oxo-5H-dibenzo [b,e]-1,4-diazepine (5)

To the diazotised solution of compound (2) (1.1250 g, 0.005*M* in 3 ml of 40% HBr and 0.4 g $NaNO_2$ at 0-5°) copper powder (0.020 g) was added, and the contents were heated cautiously over water bath for 2 hrs. The reaction mixture after cooling was filtered. The crude product was crystallised from C_2H_5OH to afford the *diazepine*

(5) (0.896 g, ca 62%), m.p. 148°, Rf 0.60 (Found, C, 54.16 : H, 3.26 ; N, 10.08 ; Br. 28.02. Calc. for $C_{13}H_9ON_2Br$ C, 53.98 ; H, 3.11 ; N, 9.69 ; Br, 27.68%). δ(DMSO) 6.15-6.50 (1H, bs, Ar – NH – Ar), 7.05-8.15 (7H, m, ArH) and 9.60 (1H, s, Ar – NH – Co –).

Acknowledgement

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Vol. LV, May 1978, pp. 474-475

Naphtho(2,3-*d*)pyrimido(2,1-*b*)(1,3)thiazines

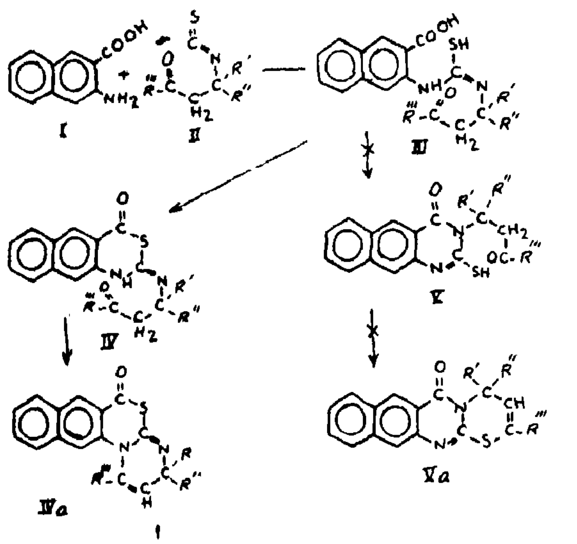
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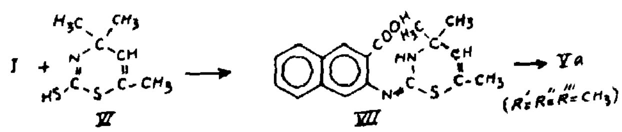
Manuscript received 2 June 1977, revised 13 December 1977, accepted 21 March 1978

Some Naphtho(2, 3-*d*) pyrimido(2, 1-*b*) (1, 3) thiazine derivatives have been synthesised by the condensation of 3-amino 2-naphthoic acid with β-isothiocyanoketones and finally cyclisation with PPA. The structure has been confirmed by analysis and i.r. studies and by comparing one of them with its isomeric benzo (*g*) (1, 3) thiazino (2, 3-*b*) quinazoline derivative prepared by an unambiguous route involving the condensation of 3-amino 2-naphthoic acid with 2-mercapto 4, 4, 6 trimethyl 4*H*, (1, 3) thiazine.

In our attempts to evolve new systems with probable biological activity around the general pattern of already known drugs, some naphtho(2,3-*d*)pyrimido(2,1-*b*)(1,3) thiazines have been synthesised by the condensation of 3-amino 2-naphthoic acid with β-isothiocyanoketones.



Isothiocyanates are known to react with amines more readily than ketones. So the first step would lead to the formation of thiourea derivative which could cyclise in two ways to give rise to IVa or Va through the formation of IV or V respectively. Contrary to our previous observations[1,2,3] where the condensation always led to the formation of the final product, in the present case the intermediate IV has been isolated. This structure, besides analytical results has been confirmed by absence of i.r. absorption band at 1650 cm^{-1} for C=O present originally in 3-amino 2-naphthoic acid. The band at 3460 cm^{-1} for –OH of COOH group also disappears. Instead two new i.r. absorption bands at 1694 cm^{-1} due to $R'''-\overset{O}{\overset{\|}{C}}-CH_2$ and 1670 cm^{-1} due to $\overset{O}{\overset{\|}{C}}-S$ appear. Moreover this intermediate IV on cyclisation with PPA gives rise to IVa. The structure of IVa has been confirmed by elemental analysis and by preparing the alternative structure Va by an unambiguous route involving the condensation of 3-amino 2-naphthoic acid with 2-mercapto 4,4,6 trimethyl 4*H*(1,3) thiazine.



It has been found that the product obtained by the former route differs from the product obtained by latter condensation in i.r., m.p., m.m.p. and tlc; thus the product obtained by the condensation of 3-amino 2-naphthoic acid and β-isothiocyanoketones and finally cyclisation with PPA may be assigned structure IV.

Further this structure finds support from earlier observations from these laboratories.[1,2,3]

Experimental

Melting points were taken in open glass capillaries in liquid paraffin bath and are uncorrected; i.r. spectra were taken in nujol on Perkin-Elmer grating i.r. spectrophotometer-621.

Condensation of 3-amino 2-naphthoic acid with 2-methyl 2-isothiocyanopentanone-4, i.e., Isolation of 2-[(1,1-Dimethyl-3-Oxobutyl)-imino]-1,2-dihydro 4H-naphtho(2,3-d)(1-3)thiazin-4-one IV($R' = R'' = R''' = CH_3$):

A mixture of 3-amino 2-naphthoic acid (1.87 g, 0.01 mol) and 2-methyl 2-isothiocyano pentanone-4 (1.57 g, 0.01 mol) was heated on an oil bath at 115-120° for 4 hours, when it changed to a hard mass.

TABLE—NAPHTHO-PYRIMIDO-THIAZINES AND THEIR INTERMEDIATES

Compound No.	R′	R″	R‴	m.p. °C	Yield %	MF	Analytical results Found %	Calculated %
IV	CH_3	CH_3	CH_3	213	78	$C_{18}H_{18}N_2O_2S$	C, 66.17 H, 6.00 N, 8.97	66.25 5.52 8.59
IVa	,,	,,	,,	345	62	$C_{18}H_{16}N_2OS$	C, 70.00 H, 5.61 N, 8.82	70.13 5.20 9.09
IV	,,	,,	C_2H_5	215	71	$C_{19}H_{20}N_2O_2S$	C, 66.89 H, 6.07	67.07 5.88
IVa	,,	,,	,,	>340	56	$C_{19}H_{18}N_2OS$	N, 8.43	8.69
IV	,,	C_2H_5	,,	224	66	$C_{20}H_{22}N_2O_2S$	C, 67.48 H, 6.51 N, 8.30	67.80 6.21 7.91
IVa	,,	,,	,,	>340	54	$C_{20}H_{20}N_2OS$	N, 8.02	8.33

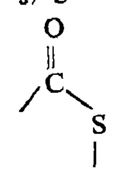
All compounds were crystallised from ethanol.

After cooling, the product was washed with a little ether and finally with water. Crystallisation from ethanol gave white needles.

2-methyl 2-isothiocyanohexanone-4 and 3-methyl 3-isothiocyanoheptanone-5 were also condensed with 3-amino-2-naphthoic acid in a similar way. The data regarding the yields of these compounds, solvent for crystallisation, m.p. and analytical results are tabulated.

1,3,3 trialkyl 3H, 6H naphtho(2,3-d) pyrimido(2,1-b)(1,3) thiazin-6-one(IVa) :

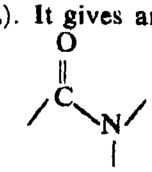
The intermediate IV(1.5 g) was mixed with PPA (prepared from 3 ml of orthophosphoric acid and 4.0 g of P_2O_5) and the contents heated on an oil bath at 140-50° for 3 hours. After cooling and diluting it with ice cold water (40 ml), the contents were basified with 5% sodium carbonate solution and collected under suction. The product was finally washed with water and crystallised. The product V(R′ = R″ = R‴ = CH_3) gives an i.r. absorption band at 1670 cm^{-1} for



The date regarding the yields of these compounds, their m.p., solvent for crystallisation and analytical results are tabulated.

Condensation of 3-amino 2-naphthoic acid with 2-mercapto 4 : 4 : 6 trimethyl 4H(1,3), thiazine, i.e., synthesis of 2,4,4, trimethyl 4H, 6H-benzo(g)(1,3) thiazino(2, 3-b)-quinazolin-6-one(Va) (R′ = R″ = R‴ = CH_3) :

A mixture of 3-amino 2.naphthoic acid hydrochloride (2.24 g, 0.01 mol) and 2-mercapto 4,4,6 trimethyl 4*H*(1,3) thiazine (1.73 g, 0.01 mol) was heated on an oil bath to 130° when there was evolution of H_2S. The temperature was raised to 150-155° and the contents heated at this temperature for 4 hours when the evolution of H_2S practically ceased. After cooling, the product was triturated with a little of ethanol and filtered. Crystallisation from ethanol gave brownish product m.p. 330°, yield being 1.6 g (52%). It gives an i.r. absorption band at 1678 cm^{-1} for



. Found C, 69. 83 ; H, 5.02 $C_{18}H_{16}N_2OS$ requires C, 70.1?, H, 5.20%.

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Chemical Constituents of the Essential Oil of *Inula royleana*

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The roots of *Inula royleana* contains 1% essential oil which on analysis by tlc and glc was found to contain eudesmol, elemol, farnesol, nerolidol, geraniol, borneol, α-terpineol, anisic alcohol, cineol, methyl heptenone, citronellal, cinnamaldehyde, β-caryophyllene, β-elemene, γ-elemene, limonene, geranyl acetate, caryophyllene oxide, β-selinene, α-selinene, δ-cadinene and unidentified compound with m.p. 145-47°.

THE roots of *Inula royleana* (compositae) are known to exhibit hypotensive activity and stimulate the peristaltic movements of intestines[1]. Earlier investigations on the roots of this species revealed the presence of alkaloids[2,4] and diterpenoids[3], presence of essential oil or its chemical constituents has not been reported so far from this species[1]. In this communication we wish to report the chemical constituents of the essential oil of this species.

Roots of *Inula royleana* (1 kg) were exhaustively extracted with light pet. ether (60-80°). The extract on concentration yielded 30 gms. of brownish viscous mass which when subjected to steam distillation gave 10gms. of the oil. The oil was found to have following physicochemical constants :

d^{30} 1.0202, n_D^{30} 1.6462, acid value 44.91 ; ester value 26.38 ester value after acetylation 128.34 and carbonyl value 22.06. The oil was then studied with the help of tlc over silica gel G using different solvent systems. Tlc revealed this oil to be of very complex nature but some of its constituents were identified by running authentic samples for comparison and using vanillin sulphuric acid and 2 : 4 dinitrophenylhydrazine as spray reagents. The following components were identified by tlc :

Eudesmol. elemol, farnesol. nerolidol, α-terpeniol, cineol, geraniol, methyl heptenone, geranyl acetate, borneol, anisic alcohol and caryophyllene oxide. The oil was then exhaustively studied by glc.

Gas liquid chromatography of the oil :

Glc of the oil was done on PE 881 having stainless steel column 6 ft. long containing SE-30 and FID. The operation was done at a programmed rate of 90-200° with 6°/min. using nitrogen as the carrier gas. The compounds in the gas chromatogram were identified by comparison of their retention times with those of the reference samples. The identified compounds along with their percentage are—

Limonene (0.76), Cineol (0.33), Methyl heptenone (0.63), Citronellal (0.16), Borneol (0.28), α-Terpeniol (0.14), Geraniol (0.79). Geranyl acetate (0.06), Caryophyllene oxide (1.37), β-Selinene (12.54), α-Selinene (4.28), β-Caryophyllene (3.70), β-Elemene (8.00), γ-Elemene (12.44), Nerolidol (6.81), Elemol (3.37). Cinnamaldehyde (1.73), Anisic alcohol (4.12), Eudesmol (1.25), Farnesol (4.43), Anisaldehyde (2.55), Alantolactone (6.34) and Isoalantolactone (4.95).

The oil was chromatographed over a silica gel column. Fractions 37-42 and 45-50 eluted with benzene yielded white solid which on crystallisation from methanol gave white crystalline compounds with m.p. 145-48° (7 mg) and 60-62°. The first compound could not be identified due to its low yield. The second compound was identified as caryophyllene oxide by mmp, co-tlc and superimposable IR with the authentic sample.

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We are thankful to Dr. C. K. Atal, Director, RRL, Jammu for his keen interest in the work, Dr. R. K. Thappa for useful suggestions. One of the authors (M. A. Q.) is thankful to CSIR, New Delhi for awarding JRF/SRF.

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Possible Antiparkinson Compounds : Part I : Synthesis of Some 2-Aryl-3-(1,3,4-thiadiazol-2-yl)-quinazolin-4(3*H*)-ones

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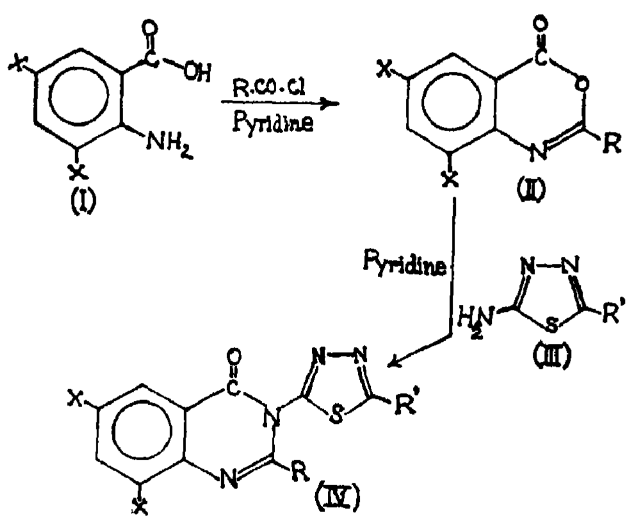
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2-Aryl-benzoxazin-4-ones (II, X=H, Br ; R=C_6H_5, $C_6H_5CH=CH$) are condensed with 2-amino-1,3,4-thiadiazoles (III, R'=H, CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, i-C_4H_9) to give 2-aryl-3-(1,3,4-thiadiazol-2-yl)quinazolin-4(3*H*)-ones (IV). These compounds have no *significant antitremorine activity*, and *they produce negligible* hypothermia.

THE thiadiazole derivatives have been reported to possess enhanced CNS depressant, anticonvulsant[1] and antiparkinson properties[2]. Further, a large number of quinazolinones have been shown to be CNS depressant[3-5], anticonvulsant[6,7] and muscle relaxants[8,9]. Tiwari and Pandey[10] have also done some work on quinazolinone derivatives. So it was worthwhile to investigate whether the compounds having both thiadiazole and quinazolinone moieties can have better pharmacological activity. Synthesis of some 2-aryl-3-(1,3,4-thiadiazol-2-yl)quinazolin-4(3*H*)-ones and assessment of their antiparkinsonism activity are described in this paper.

The synthesis was accomplished along the following route :



Experimental

2-Aryl-benzoxazinones(II) – A mixture of anthranilic acid or 3,5-dibromoanthranilic acid[11] (0.01 mole) and the appropriate acid chloride (0.02 mole) was stirred in anhydrous pyridine (35 ml) for 2 hrs. The reaction was exothermic, therefore cooling was also done occasionally during stirring. The mixture was diluted with water, the separated solid filtered, washed with 5% sodium bicarbonate solution, and finally recrystallised from alcohol.

2-Amino-5-alkyl-1,3,4-thiadiazoles(III) – These were prepared by the method given by Funatsukuri *et al.*[12]. A mixture of the alkyl carboxylic acid (0.1 mole) and thiasemicarbazide (0.1 mole) in excess of sulphuric acid (A.R.) was refluxed for 6 hrs. Subsequently, the mixture was cooled, poured into excess of ice water, and neutralised with ammonia to precipitate the product.

2-Aryl-3-(5-alkyl-1,3,4-thiadiazol-2-yl)-quinazolin-4(3H)-ones (IV) – The benzoxazinone(II) (0.005 mole) and 2-amino-5-alkyl-1,3,4-thiadiazole(III) (0.005 mole) were refluxed together in pyridine (20 ml) for about 6 hrs. Subsequently, after cooling to room temperature it was poured in a mixture containing conc. HCl (100 ml) and crushed ice (100 g), when the solid product was separated out. The solid was filtered at the pump and washed repeatedly with cold water. It was dried and crystallised from alcohol or alcohol water.

Various quinazolinones(IV) thus synthesised in 55-60% yield are listed in Table I.

Pharmacology :

Six compounds (marked by asterisks in Table I) were subjected for their toxicity test[13] (determination of ALD_{50} values) and antitremorine activity. All the compounds were well tolerated by albino mice even up to the doses of 1000 mg/kg without any toxic menifestations. This observation indicated the non-toxicity of these quinazolinones.

For antitremor activity, the albino mice of either sex were chosen. The compound under screening was given intraperitoneally. One hour after the drug administration, oxo-tremorine

(dissolved in water) was given to mice intraperitoneally. None of the compound was found to possess significant antitremorine activity.

TABLE—1 : 2-ARYL-3-(1,3,4-THIADIAZOL-2-YL)-QUINAZOLIN-4-(3*H*)-ONES (IV)†

Sl. N.	R	R′	X	m.p.°C‡
a.	$-C_6H_5$	$-H$	H	250
b.*	$-C_6H_5$	$-CH_3$	H	217
c.	$-C_6H_5$	$-CH_2CH_3$	H	210
d.	$-C_6H_5$	$-n\text{-}C_3H_7$	H	185
e.*	C_6H_5	$(CH_3)_2>CH-$	H	220
f.*	$-C_6H_5$	$-n\text{-}C_4H_9$	H	188
g.	$-C_6H_5$	$(CH_3)_2>CH-CH_2-$	H	200
h.*	$C_6H_5CH=CH-$	$-H$	H	243
i.	$C_6H_5CH=CH-$	$-CH_3$	H	186
j.	$C_6H_5CH=CH-$	$-CH_2CH_3$	H	210
k.	$C_6H_5CH=CH-$	$-n\text{-}C_3H_7$	H	189
l.	$C_6H_5CH=CH-$	$(CH_3)_2>CH-$	H	195
m.*	$C_6H_5CH=CH-$	$-n\text{-}C_4H_9$	H	191
n.	$C_6H_5CH=CH-$	$(CH_3)_2>CH-CH_2-$	H	205
o.	$-C_6H_5$	$-H$	Br	211
p.*	$-C_6H_5$	CH_3	Br	196
q.	$-C_6H_5$	$-CH_2-CH_3$	Br	220
r.	$-C_6H_5$	$-n\text{-}C_3H_7$	Br	190
s.	$-C_6H_5$	$(CH_3)_2>CH-$	Br	240
t.	$-C_6H_5$	$-n\text{-}C_4H_9$	Br	193
u.	$-C_6H_5$	$(CH_3)_2>CH-CH_2-$	Br	200

† All the compounds gave correct analysis for nitrogen.
‡ The melting points are uncorrected.

The compounds produced negligible hypothermia (not more than 1.0° at 200 i.p.). The SMA also decreased by slight degree.

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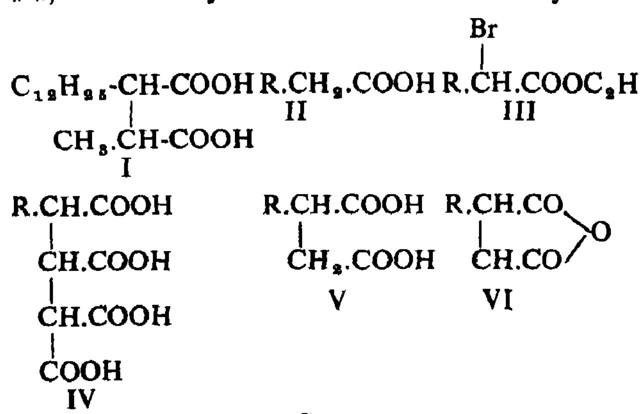
Potential Antitubercular Drugs : II. Synthesis of Some Mono-N-Arylamides of Alkylsuccinic Acids†

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The preparation and characterisation of some mono-N-arylamides of *n*-hexyl, *n*-decyl, *n*-dodecyl and *n*-hexadecyl succinic acids are described. The antitubercular activity of these acids are also reported.

THE observation by Barry[1] that rocelli acid(I), isolated from the Lichen *lecanora sordida* possesses tuberculostatic properties *in vitro* prompted him and his co-workers[2,3] to synthesise a number of alkyl substituted succinic acids and their derivatives with a view to study their antitubercular activity. The results were encouraging and the compounds were found to possess, as anticipated, antitubercular activity in various degrees. These authors could also make a rough correlation of antitubercular activity with the number of carbon atoms in the alkyl chain. Somewhat similar studies were carried out later by Joshi and co-workers[4] with alkylaryl succinic acids.

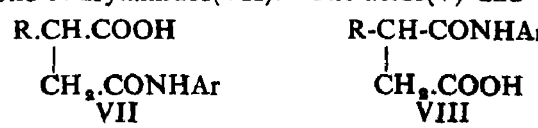
In view of activity exhibited by such succinic acids and their derivatives it was considered worthwhile to undertake the synthesis of some mono-N-arylamides(VII) of a few alkyl succinic acids(V, *a-d*) and to study their antitubercular activity.



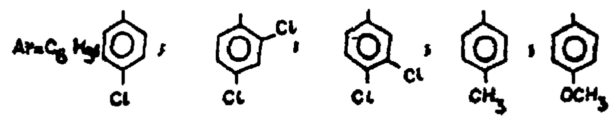
a, R = n-$C_{10}H_{21}$
b, R = n-$C_{12}H_{25}$
c, R = n-$C_{16}H_{33}$
d, R = n-C_6H_{13}

n-Hexylsuccinic acid (V, *d*) was prepared according to Higginbotham and Lapworth[5]. The other succinic acids were prepared by the method due to Bischoff[6] (Bentley, Perkin & Thorpe[7]). The starting materials were lauric, myristic and stearic acids (II, *a-c*) which were brominated at the α-position by Hell-Volhard-Zelinsky method. The bromo acids were not isolated, rather the intermediate acid bromides were esterified *in situ* when the corresponding esters(III, *a-c*) were obtained. The ethyl esters of the tricarboxylic acids(IV, *a-c*) were then readily obtained from the foregoing crude bromoesters by reaction with diethyl sodiomalonate, Hydrolysis to the tri-acids followed by thermal decarboxylation gave the succinic acids(V, *a-c*). Incidentally, it is interesting to note that all the three tricarboxylic acids have the same decomposition temperature as that (m.p.) of malonic acid. The overall yield of the succinic acids(V) was fairly good in each case.

The desired mono-N-arylamides were prepared from these acids *via* their anhydrides(VI, *a-d*) which were readily obtained by heating the corresponding acid(V) with excess of acetyl chloride. The anhydrides when heated with one molecular proportion of the appropriate primary aromatic amine in benzene solution readily gave the corresponding mono-N-arylamides(VII). The acids(V) and



R = C_6H_{13} ; $C_{10}H_{21}$; $C_{12}H_{25}$; $C_{16}H_{33}$



† This work constituted part fulfilment of Ph.D. Thesis of M.M.T. under Patna University
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TABLE—1 ALKYL SUCCINIC ACIDS(V) AND THEIR ANHYDRIDES(VI)

(A) **The Acids** R–CH–COOH
 |
 CH_2.COOH

	Compound	% Yield	M. P. and crystalline nature	Mol. formula	Analysis Found		Required	
1.	*n*-Hexylsuccinic acid	65	87° glistening plates from methanol	$C_{10}H_{18}O_4$	C 59.65 H 9.01		C 59.00	H 8.91
2.	*n*-Decylsuccinic acid	60	94-95 plates from acetic acid	$C_{14}H_{26}O_4$	C 65.19 H 10.12		C 65.11	H 10.07
3.	*n*-Dodecylsuccinic acid	80	101° colourless plates from AcOH	$C_{16}H_{30}O_4$	C 67.23 H 10.15		C 67.15	H 10.41
4.	*n*-Hexadecylsuccinic acid	75	106° colourless plates	$C_{20}H_{38}O_4$	C 70.47 H 11.51		C 71.15	H 11.11
	(B) The Anhydrides R–CH–CO–O–CO–CH_2 (cyclic: R–CH–CO⟩O, CH_2–CO)							
5.	*n*-Hexylsuccinic anhydride	55	57° liquid, solidified on cooling	$C_{10}H_{16}O_3$	C 65.45 H 8.98		C 65.21	H 8.70
6.	*n*-Decylsuccinic anhydride	55	68-69° plates pet. ether	$C_{14}H_{24}O_3$	C 70.15 H 10.31		C 70%	H 10%
7.	*n*-Dodecylsuccinic anhydride	60	75° colourless from petroleum ether	$C_{16}H_{28}O_3$	C 71.98 H 10.81		C 71.64	H 10.45
8.	*n*-Hexadecylsuccinic anhydride	59	78° colourless from petroleum ether	$C_{20}H_{36}O_3$	C 74.12 H 11.65		C 74.08	H 11.11

TABLE—2

R–CH–COOH
 CH_2–CONH

Sl. no.	Name of the compound	% Yield	m.p.°	Molecular Formula	Analysis Found	Analysis Required	Minimum inhibitory concentration mcg/ml
1.	Monoanilide of *n*-hexylsuccinic acid	57	114	$C_{16}H_{23}NO_3$	C 69.45 H 8.52 N 5.43 eq. wt. 272.5	C 69.31 H 8.3 N 5.05 eq. wt. 277.00	100.00
2.	Mono *p*-chloroanilide of *n*-hexylsuccinic acid	32	123	$C_{16}H_{22}ClNO_3$	C 62.00 H 7.27 N 4.81 eq. wt. 309.2	C 61.63 H 7.06 N 4.49 eq. wt. 311.5	10.00
3.	Mono 2, 4-dichloroanilide of *n*-hexylsuccinic acid	26	97	$C_{16}H_{21}Cl_2NO_3$	C 55.65 H 6.18 N 4.32 eq. wt. 339.4	C 55.49 H 6.07 N 4.05 eq. wt. 346.0	100.00
4.	Mono 3, 4-dichloroanilide of *n*-hexylsuccinic acid	29	117	,, ,,	C 55.81 H 6.23 N 4.32 eq. wt. 341.1	,, ,,	100.00
5.	Mono *p*-methylanilide of *n*-hexylsuccinic acid	38	120	$C_{17}H_{25}NO_3$	C 70.23 H 8.8 N 5.06 eq. wt. 285.5	C 70.07 H 8.65 N 4.81 eq. wt. 291.0	0.10
6.	Mono *p*-methoxyanilide of *n*-hexylsuccinic acid	65	131	$C_{17}H_{25}NO_4$	C 66.76 H 8.37 N 4.81 eq. wt. 310.1	C 66.45 H 8.14 N 4.56 eq. wt. 307.0	100.00
7.	Monoanilide of *n*-decylsuccinic acid	57	106	$C_{20}H_{31}O_3N$	C 72.21 H 9.63 N 4.58 eq. wt. 328.5	C 72.07 H 9.37 N 4.20 eq. wt. 333.0	400.00
8.	Mono *p*-chloroanilide of *n*-decylsuccinic acid	33	120	$C_{20}H_{30}ClO_3N$	C 65.52 H 8.34 N 4.01 eq. wt. 360.7	C 65.30 H 8.16 N 3.81 eq. wt. 367.5	1.00
9.	Mono 2,4-dichloroanilide of *n*-decylsuccinic acid	18	107	$C_{20}H_{29}Cl_2O_3N$	C 60.01 H 7.43 N 3.61 eq. wt. 394.2	C 59.70 H 7.21 N 3.48 eq. wt. 402.0	10.00
10.	Mono 2,5-dichloroanilide of *n*-decylsuccinic acid	52	104	,, ,,	C 60.11 H 7.35 N 3.58 eq. wt. 399.8	C 59.70 H 7.21 N 3.48 eq. wt. 402.0	1.00
11.	Mono *p*-methylanilide of *n*-decylsuccinic acid	43	121	$C_{21}H_{33}O_3N$	C 72.85 H 9.63 N 4.40 eq. wt. 351.5	C 72.63 H 9.51 N 4.03 eq. wt. 347.0	1.00
12.	Mono *p*-methoxyanilide of *n*-decylsuccinic acid	35	131	$C_{21}H_{33}O_4N$	C 69.76 H 9.51 N 4.04 eq. wt. 368.0	C 69.4 H 9.09 N 3.85 eq. wt. 365.0	0.10

(Table 2 Contd.)

13. Monoanilide of *n*-dodecylsuccinic acid	38	126	$C_{22}H_{35}O_3N$	C 73.51 H 10.12 N 4.13 eq. wt. 363.7	C 73.18 H 9.7 N 3.87 eq. wt. 361.0	400.00
14. Mono *p*-chloroanilide of *n*-dodecylsuccinic acid	46	122	$C_{22}H_{34}ClO_3N$	C 67.10 H 8.31 N 3.81 397.5 (eq. wt.)	C 66.76 H 8.60 N 3.54 eq. wt. 395.5	10.00
15. Mono 3, 4-dichloroanilide of *n*-dodecylsuccinic acid	30	119	$C_{22}H_{33}Cl_2O_3N$	C 61.76 H 7.48 N 3.47 eq. wt. 428	C 61.39 H 7.07 N 3.26 eq. wt. 430	10.00
16. Mono p-methylanilide of *n*-dodecylsuccinic acid	32	132	$C_{23}H_{37}O_3N$	C 73.96 H 9.65 N 4.08 eq. wt. 388.00	C 73.64 H 9.87 N 3.73 eq. wt. 375.00	100.00
17. Mono *p*-methoxyanilide of *n*-dodecylsuccinic acid	31	140	$C_{23}H_{37}O_4N$	C 70.84 H 9.33 N 3.84 eq. wt. 392.5	C 70.58 H 9.46 N 3.58 eq. wt. 391.00	100.00
18. Mono *m*-chloroanilide of *n*-dodecylsuccinic acid	15	87.88	$C_{22}H_{34}ClO_3N$	C 67.17 H 8.25 N 3.81 eq. wt. 401.27	C 66.76 H 8.50 N 3.54 eq. wt. 395.50	–
19. Monoanilide of *n*-hexadecylsuccinic acid	26	144	$C_{26}H_{43}O_3N$	C 75.22 H 10.04 N 3.62 eq. wt. 427.30	C 74.85 H 10.31 N 3.36 eq. wt. 417.00	400.00
20. Mono m-chloroanilide of *n*-hexadecylsuccinic acid	35	94	$C_{26}H_{42}ClO_3N$	C 69.47 H 9.02 N 3.37 eq. wt. 449.8	C 69.10 H 9.30 N 3.10 eq. wt. 451.5	–
21. Mono *o*-chloroanilide of *n*-hexadecylsuccinic acid	22	119	,, ,,	C 69.51 H 9.05 N 3.49 eq. wt. 449.0	,, ,,	400.00
22. Mono *p*-chloroanilide of *n*-hexadecylsuccinic acid	35	108	$C_{26}H_{42}ClO_3N$	C 69.52 H 9.14 N 3.46 eq. wt. 449.8	,, ,,	10.00
23. Mono 3, 4,-dichloroanilide of *n*-hexadecylsuccinic acid	48	97	$C_{26}H_{41}Cl_2O_3N$	C 64.60 H 8.25 N 3.21 eq. wt. 488.40	C 64.21 H 8.41 N 2.88 eq. wt. 486.00	100.00
24. Mono *p*-methylanilide of *n*-hexadecylsuccinic acid	39	128	$C_{27}H_{45}O_3N$	C 75.47 H 10.09 N 3.62 eq. wt. 427.30	C 75.16 H 10.44 N 3.25 eq. wt. 431.00	10.00
25. Mono *p*-methoxyanilide of *n*-hexadecylsuccinic acid	31	126	$C_{27}H_{45}O_4N$	C 72.86 H 9.82 N 3.52 eq. wt. 449.2	C 72.47 H 10.07 N 3.13 eq. wt. 447.00	100.00

the anhydrides(VI) prepared are listed in Table 1. The mono-N-arylamides of the succinic acid are listed in Table 2.

It is obvious that the anhydride(VI) can give rise to two isomeric monoarylamides, (VII) and (VIII). Only one monoarylamide was isolated in each case. Higson and Thorpe[8] have, without any proof, assigned the structure(VIII, $R = C_6H_{13}$; $Ar = C_6H_5$) to the anilic acid derived from(VI, *d*). On the other hand, Bhide and Ghate[9] have conclusively proved that the mono-amide derived from phenethyl succinic anhydride(VI, $R = C_6H_5-CH_2CH_2-$) isrepresented by(VII, $R = C_6H_5-CH_2CH_2$; $Ar = H$). A consideration of the mechanism of formation of the amides from anhydrides would reveal that the formation of (VII) would be favoured slightly over that of (VIII) if the alkyl group is large enough to cause steric hindrance.

The compounds prepared have been tentatively assigned the structure(VII).

Bactereological screening and results

The *in vitro* tuberculostatic screening of the compounds was carried out in Youman's liquid medium at *p*H, 7.0. *Mycobacterium tuberculosis* H37RV *var hominis* was used as the test organism. The medium was incubated for four weeks at 37° prior to inoculation of the drug. The drug was introduced at various dilutions from 400 mcg/ml to 0.1 mcg/ml. The minimum inhibitory concentration is given in Table 2. The standards used for comparison were isonicotinic acid hydrazide(INH) and *p*-aminosalicylic acid (PAS).

It has been found that the arylamides of *n*-hexyl succinic acid have the highest activity compared to the corresponding amide of the other alkyl succinic acids. Amongst the arylamides of any particular succinic acid the *p*-chloro-, *p*-methyl- and 2,4-dichloro anilides are the most potent.

Experimental

All m.ps. are uncorrected and were taken in sulphuric acid bath.

Tetradecane-1,1,2-tricarboxylic acid

To an alcoholic solution of sodium ethoxide (1.15 g Na in 15 ml ethanol), diethylmalonate (8 g) was added followed by a gradual addition of ethyl-bromomyristate (17.05 g). The mixture was thereafter refluxed for two hours and then allowed to cool. An aqueous alcoholic solution of sodium hydroxide (4.0 g NaOH in 20 ml of 50% ethanol)

was now added and the mixture refluxed for 6 hours. Removal of alcohol followed by addition of water and acidification with hydrochloric acid liberated the tricarboxylic acid as a pale yellow solid mass. It was obtained as colourless microneedles m.p. 135°(decomp.) from dilute acetic acid, yield 12.5 g.

Found C, 61.56% ; H, 9.67%

$C_{17}H_{30}O_6$ requires C, 61.81 ; H, 9.09%

All other tricarboxylic acids were prepared by the similar method. The other tricarboxylic acids also had m.p. (decomp.) 135°.

n-Dodecylsuccinic acid

The foregoing tricarboxylic acid was heated at 140° till evolution of carbon dioxide ceased completely (30 minutes). The solid mass obtained on cooling, was crystallized from acetic acid as colourless plates m.p. 101°, yield 80%.

n-Dodecylsuccinic anhydride

n-Dodecyl succinic acid (0.033 mole. 9.5 g) was refluxed gently with excess of acetylchloride (8 g) for two hours. Excess of acetylchloride was removed under reduced pressure. The anhydride obtained as a solid mass on cooling, was crystallized from petroleum ether as colourless plates. m.p. 75°, yield 60%.

Found C. 71.98% ; H. 10.81%

$C_{16}H_{28}O_3$ req. C. 71-64% ; H, 10.45%

Monoanilide of n-dodecylsuccinic acid

To a solution of *n*-dodecylsuccinic anhydride (0.01 mole) in dry benzene (10 ml), a solution of freshly distilled aniline (0.01 mole) in benzene (10 ml) was added and refluxed mildly for half and an hour. The reaction mixture was cooled, taken up in sodium bicarbonate solution. The benzene layer was separated and rejected. The aqueous layer was acidified with hydrochloric acid. The solid obtained was filtered and crystallized from dilute alcohol in fine microneedles, m.p. 126°. yield 33%. The aqueous filtrate was evaporated to dryness on steam bath. The residue was heated with dry ethanol. No pure organic compound could be isolated from this ethanolic solution.

Found C, 73.51% ; H, 10.12% ; N, 4.13%

$C_{22}H_{35}O_3N$ req. C, 73.18% ; H. 9.70% ; N, 3.88%

All other anilides were prepared in the similar way.

Acknowledgement

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Synthesis and Fungitoxicity of Some 5-Substituted-3-Polynitrophenyl Rhodanines

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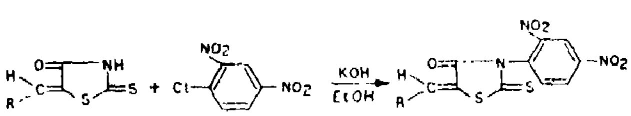
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Forty-four 5-substituted-3-polynitrophenyl rhodanines have been prepared by the condensation of reactive halogenonitrobenzenes and 5-substituted rhodanine in the presence of an alkali. They have been characterised and tested for their antifungal activity against *Helminthosporium sativum*, *Alternaria tenuis*, *Aspergillus niger* and *Fusarium oxysporum* by spore germination method. A relation between fungitoxicity and structure has also been established.

2-Mercapto-4-thiazolidones or rhodanines possess insecticidal and fungicidal properties[1]. Recently N-substituted-4-thiazolidones have been reported to possess anthelmintic[2], nematocidal[3], pesticidal[4] and fungicidal[5,6] activity. Vander Kerk[7] and Brown[6] reported that 3-substituted aryl rhodanines are much more fungitoxic than the unsubstituted ones. A few 3-halogenonitrophenyl rhodanine were obtained by Gupta and Dureja[8] by the condensation of halogenonitrobenzenes with 2-mercapto-4-thiazolidone, in ethanolic solution in the presence of potassium hydroxide. A study of literature reveals that only a few rhodanines with substituents present at position 5 have been studied. On the basis of these observations. it was thought of interest to prepare a large number of 5-substituted-polynitrophenyl rhodanines having halogen, nitro and methyl groups as substituents at different positions in the 3-phenyl ring, with a view to test their effect on fungitoxicity and to establish a relation between structure and activity.

5-Substituted-3-polynitrophenyl rhodanines(III) have been obtained by the condensation of halogenonitrobenzene(II) with 5-suhstituted rhodanine(I) in ethanolic solution in the presence of potassim hydroxide.



(I) (II) (III)

Thus sixteen halogenonitrobenzenes have been condensed with 5-substituted rhodanine to give the corresponding 5-substituted-3-polynitrophenyl rhodanines (Tables 1,2 and 3).

The I. R. Spectra of these compounds have also been recorded and are in complete agreement with their structures.

These compounds were tested for their antifungal activity against *Helminthosporium sativum*, *Alternaria tenuis*, *Aspergillus niger* and *Fusarium oxysporum* by spore germination method[9] (Tables 1, 2 and 3). The percentage inhibition of spores at 10 ppm have been recorded.

Experimental

General method for the preparation of 5-substituted rhodanines[10] *:*

To a solution of 0.6 mole of aldehyde and 0.6 mole of rhodanine[11] in 400 c.c. of hot glacial acetic acid, 150 g. of fused sodium acetate was added and the mixture boiled for one and a half hour with occasional shaking. The substituted rhodanine soon separates out as orange yellow crystals. The whole mass was poured into 3 litres of water. The crystals that separated were filtered and washed well with water, followed by little alcohol and ether, yield 96% The product was recrystallised from acetone.

General method for the preparation of 5-substituted-3-polynitrophenyl rhodanines :

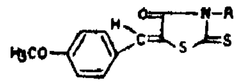
A solution of halogenonitrobenzene (0.01*M*) and potassium hydroxide (0.01*M*) in ethanol was added dropwise to a solution of 5-substituted rhodanine (0.01M) in ethanol (10 ml). The mixture was then refluxed for about four to five hours. On cooling the product was filtered, washed with water and crystallised out of acetone.

Rhodanines so obtained are insoluble in water and soluble in acetone. Their melting points, yield, analytical data and fungitoxicity have been recorded in Tables 1, 2 and 3.

Results and Discussion

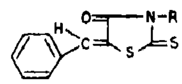
5-Substituted-3-polynitrophenyl rhodanines have been found to possess marked fungitoxicity at 10 ppm level. Halogen and/or nitro group when placed at ortho and/or para position to the 3-phenyl linkage, enhances fungitoxicity to a greater extent. A halogen atom at meta position decreases the

TABLE 1—5-ANISAL-3-POLYNITROPHENYL RHODANINES



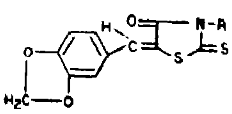
Sl. No.	R	M.P. °C	Yield %	Mol. Formula	% Nitrogen Found	% Nitrogen Reqd.	% Sulphur Found	% Sulphur Reqd.	Percentage inhibition of spores at 10 ppm HS	AT	AN	FO
1.	2,4-DNP	140	75	$C_{17}H_{11}N_3O_6S_2$	9.85	10.07	15.10	15.84	28	30	25	28
2.	2,6-DNP	150	78	$C_{17}H_{11}N_3O_6S_2$	9.82	10.07	15.05	15.34	32	32	30	35
3.	2,4,6-TNP	225	70	$C_{17}H_{10}N_4O_8S_2$	11.90	12.12	13.62	13.85	40	50	38	38
4.	2-Chloro-4,6-DNP	195	80	$C_{17}H_{10}N_3O_6ClS_2$	9.10	9.30	14.02	14.17	36	66	52	46
5.	2-Bromo-4,6-DNP	135	75	$C_{17}H_{10}N_3O_6BrS_2$	8.26	8.47	12.62	12.90	20	18	22	6
6.	3-Chloro-4,6-DNP	155	80	$C_{17}H_{10}N_3O_6ClS_2$	9.05	9.30	14.00	14.17	10	15	19	18
7.	4-Chloro-2,6-DNP	178	70	$C_{17}H_{10}N_3O_6ClS_2$	9.08	9.30	13.96	14.17	15	19	25	15
8.	2-Methyl-4,6-DNP	130	78	$C_{18}H_{13}N_3O_6S_2$	9.50	9.74	14.64	14.85	23	26	20	10
9.	3-Methyl-4,6-DNP	146	85	$C_{18}H_{13}N_3O_6S_2$	9.45	9.74	14.62	14.85	28	31	22	18
10.	4-Methyl-2,6-DNP	99	65	$C_{18}H_{13}N_3O_6S_2$	9.60	9.74	14.63	14.85	32	28	21	24
11.	3-Methyl-2,4,6-TNP	155	65	$C_{18}H_{12}N_4O_8S_2$	11.51	11.76	13.23	13.44	24	25	28	20
12.	2,3-Dichloro-4,6-DNP	125	72	$C_{17}H_9N_3O_6Cl_2S_2$	8.40	8.64	13.00	13.17	30	38	25	31
13.	2,5-Dichloro-4,6-DNP	75	70	$C_{17}H_9N_3O_6Cl_2S_2$	8.38	8.64	12.95	13.17	35	33	23	38
14.	2-Chloro-5-methyl-4,6-DNP	80	70	$C_{18}H_{12}N_3O_6ClS_2$	8.80	9.02	13.48	13.74	18	25	13	00
15.	2-Bromo-5-methyl-4,6-DNP	95	65	$C_{18}H_{12}N_3O_6BrS_2$	8.48	8.23	12.32	12.55	15	18	10	5
16.	3-Chloro-2-methyl-4,6-DNP	148	68	$C_{18}H_{12}N_3O_6ClS_2$	8.85	9.02	13.54	13.74	8	6	14	10

TABLE 2—5-BENZAL-3-POLYNITROPHENYL-RHODANINES



Sl. No.	R	M.P. °C	Yield %	Mol. Formula	% Nitrogen Found	% Nitrogen Reqd.	% Sulphur Found	% Sulphur Reqd.	Percentage inhibition of spores at 10 ppm HT	AT	AN	FO
1.	2,4-DNP	180	80	$C_{16}H_9N_3O_5S_2$	10.65	10.85	16.25	16.53	22	20	25	10
2.	2,6-DNP	105	75	$C_{16}H_9N_3O_5S_2$	10.68	10.85	16.20	16.53	28	25	23	12
3.	2,4,6-TNP	190	75	$C_{16}H_8N_4O_7S_2$	12.65	12.96	14.60	14.81	35	28	30	10
4.	2-Chloro-4,6-DNP	80	82	$C_{16}H_8N_3O_5ClS_2$	9.75	9.96	15.32	15.11	31	25	28	10
5.	2-Bromo-4,6-DNP	175	70	$C_{16}H_8N_3O_5BrS_2$	8.85	9.01	13.52	13.73	25	15	20	00
6.	3-Chloro-4,6-DNP	85	78	$C_{16}H_8N_3O_5ClS_2$	9.72	9.96	14.87	15.11	28	26	30	25
7.	4-Chloro-2,6-DNP	184	70	$C_{16}H_8N_3O_5ClS_2$	9.68	9.96	14.90	15.11	30	30	32	20
8.	2-Methyl-4,6-DNP	178	80	$C_{17}H_{11}N_3O_5S_2$	10.20	10.47	15.72	15.96	15	15	10	00
9.	3-Methyl-4,6-DNP	168	85	$C_{17}H_{11}N_3O_5S_2$	10.22	10.47	15.80	15.96	30	26	16	28
10.	4-Methyl-2,6-DNP	170	65	$C_{17}H_{11}N_3O_5S_2$	10.34	10.47	15.67	16.96	21	23	14	25
11.	3-Methyl-2,4,6-TNP	90	72	$C_{17}H_{10}N_4O_7S_2$	12.24	12.55	14.07	14.35	18	20	23	8
12.	2,3-Dichloro-4,6-DNP	95	80	$C_{16}H_7N_3O_5Cl_2S_2$	9.00	9.21	13.86	14.03	38	35	30	30
13.	2,5-Dichloro-4,6-DNP	145	80	$C_{17}H_{11}N_3O_5Cl_2S_2$	10.18	10.47	15.67	15.96	31	30	35	35
14.	2-Chloro-5-methyl-4,6-DNP	92	85	$C_{17}H_{10}N_3O_5ClS_2$	9.34	9.64	14.36	14.69	26	21	25	10
15.	2-Bromo-5-methyl-4,6-DNP	102	75	$C_{17}H_{10}N_3O_5BrS_2$	8.50	8.75	13.04	13.33	16	10	15	00
16.	3-Chloro-2-methyl-4,6-DNP	176	70	$C_{17}H_{10}N_3O_5ClS_2$	9.46	9.64	14.48	14.69	4	8	10	00

TABLE 3—5-PIPERONAL-3-POLYNITROPHENYL RHODANINES



Sl. No.	R	M.P. °C	Yield %	Mol. Formula	% Nitrogen Found	% Nitrogen Reqd.	% Sulphur Found	% Sulphur Reqd.	Percentage inhibition of spores at 10 ppm HS	AT	AN	FO
1.	2,4-DNP	195	80	$C_{17}H_9N_3O_7S_2$	9.50	9.74	14.60	14.85	28	20	23	10
2.	2,6-DNP	220d	85	$C_{17}H_9N_3O_7S_2$	9.47	9.74	14.56	14.85	31	33	26	16
3.	2,4,6-TNP	283	70	$C_{17}H_8N_4O_9S_2$	11.50	11.76	13.16	13.44	36	50	15	18
4.	2-Chloro-4,6-DNP	220	60	$C_{17}H_8N_3O_7ClS_2$	8.80	9.02	13.50	13.74	25	28	30	8
5.	2-Bromo-4,6-DNP	84	65	$C_{17}H_8N_3O_7BrS_2$	8.06	8.23	12.78	12.55	15	20	18	4
6.	3-Chloro-4,6-DNP	185	80	$C_{17}H_8N_3O_7ClS_2$	9.23	9.02	13.52	13.74	21	24	15	0
7.	4-Chloro-2,6-DNP	115d	76	$C_{17}H_8N_3O_7ClS_2$	9.25	9.02	13.45	13.74	32	16	18	10
8.	2-Methyl-4,6-DNP	215d	80	$C_{18}H_{11}N_3O_7S_2$	9.12	9.44	14.20	14.88	15	10	10	0
9.	4-Methyl-2,6-DNP	280d	65	$C_{18}H_{11}N_3O_7S_2$	9.18	9.44	14.26	14.38	20	24	13	0
10.	2,3-Dichloro-4,6-DNP	235d	75	$C_{17}H_7N_3O_7Cl_2S_2$	8.21	8.40	12.52	12.80	25	28	21	6
11.	2-Chloro-5-methyl-4,6-DNP	250d	80	$C_{18}H_{10}N_3O_7ClS_2$	8.58	8.76	13.06	13.33	28	20	25	10
12.	3-Chloro-2-methyl-4,6-DNP	118d	75	$C_{18}H_{10}N_3O_7ClS_2$	8.52	8.76	13.10	13.33	26	25	18	10

DNP and TNP refers to dinitrophenyl and trintrophenyl respectively. All melting points are uncorrected. Satisfactory C, H analysis have been obtained for all these compounds.
HS, AT, AN and FO refers to *Helminthosporium sativum*, *Alternaria tenuis*, *Aspergillus niger* and *Fusarium oxysporum* respectively.

fungitoxicity. A methyl group at ortho or meta position in 3-phenyl ring usually decreases fungitoxicity. However, at the para position, a methyl group enhances fungitoxicity.

Rhodanines carrying anisal group at position-5 are more fungitoxic in comparison to other rhodanines carrying piperonal or benzal group.

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A Novel pH Profile in the Reactions of Amines by Chloramine-T

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The pH profile in the reactions of aniline, p-chloro aniline and m-chloro aniline with CAT in pure aqueous medium has been reported for the first time. The enhanced reactivity around pH 4.5 has been attributed to the presence of hypochlorous acid as the species. Reactions have been observed to proceed through initial N-Chlorination, which then undergoes rearrangement to give halobenzene till pH 8 and beyond pH 10 hydrolysis and condensation to give azo compounds.

OUR interest in the chlorination of aromatic amines by CAT and NCS was mainly because of measurable rates of chlorination with these reagents. We have recently reported[1] our work on chlorination of aromatic amines by CAT in aqueous acetic acid at varying acidities. We have also recently reported[2] the oxidation of aromatic amines by CAT in alkaline medium where the products are azobenzenes. The present study involves an investigation of the pH profile of CAT reaction of aniline, p-chloro aniline and meta chloro aniline in aqueous system up to pH 6.85 and in aqueous ethanol system at pH 8-12. There is minimal contribution due to solvent effect and there is no perceptible solvent oxidation as well under the conditions.

Second order rate constants have been given in Table 1 for aniline, p-chloro aniline and m-chloro aniline. It is clear that the pH dependence is not linear in the total pH range, and the rate maximum occurs at pH 4.5. In the first sight it may look as if aniline, p-chloro aniline and m-chloro aniline having similar H^+ dependence would have increased rates of chlorination as competing protonation becomes less. But this would have resulted in a clean steep pH profile. To us it appears that the CAT species is more important and is sensitive to pH. Several species of CAT are current in literature :

TABLE 1

SECOND ORDER RATE CONSTANTS FOR ANILINE, p-CHLORO ANILINE AND m-CHLORO ANILINE AT VARIOUS pH.

Temp : 35° aqueous medium.

	k_2 l.mole^{-1}sec^{-1}							
Substrate pH→	1.6	2.2	4.5	5.4	6.85	8*	10*	12*
Aniline	0.035	0.25	4.1	1.09	0.11	0.006779	0.00595	0.0059
p-chloro aniline	0.041	0.28	4.99	2.22	0.17	0.001951	0.00345	0.0042
m-chloro aniline	0.052	0.25	2.34	1.25	0.167	0.001321	0.00258	0.0025

*All the experiments at pH 8, pH 10 and pH 12 have been done at 60° and in 10% aqueous ethanol (ethanol : water : 10 : 90 V/V) due to solubility consideration. Even then it is clearly seen that the rates are much lower in general.

(1) CAT(sodium salt) (2) CAT(RNHCl) (3) DCT (4) HOCl (5) H_2O^+Cl. The hydrolysed species (RNHCl) are important till pH 2.2 and at 6.8 and the near identical rates point to the same type of species. Higuchi[3] and Mahadevappa[4] have obtained evidences for DCT formation in the pH range 4-7 and 3-4 in the CAT-p-cresol reaction and in the conductometric measurements respectively. But the best kinetic evidence for DCT formation and chlorination through it would be a second order dependence on CAT, as seen from the equilibrium :

$$2\ \text{CAT} \rightleftharpoons \text{DCT} + \text{TSA}$$

The order with respect to CAT has been checked by varying the concentrations of CAT at pH 4.5. For a three-fold increase in the concentration of CAT the first order rate constant (k_1) almost remained constant indicating the first order dependence on CAT (Table 2). This constancy of the first order rate constants conclusively establishes the first order dependence with respect to CAT. This rules out any DCT formation under our conditions. Hence the only acceptable species in the pH range

TABLE—2

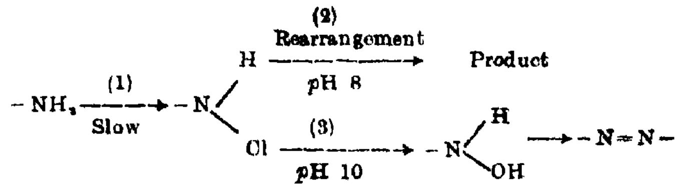
VARIATION OF CONCENTRATION OF CAT AT pH 4.5 IN AQUEOUS MEDIUM. [ANILINE]=0.005M, TEMP : 35°

10^4[CAT]	$10^3 k_1$ sec^{-1}
4.395	19.19
6.45	19.19
7.97	21.41
8.78	20.51
10.93	21.41

5 is the hypochlorous acid. This agrees well with the work of Mushran[5] in the oxidation of primary alcohols by CAT at pH 4.5.

We had earlier postulated on the basis of our kinetic investigation at and below pH 1.7 that there is direct halogen transfer to the amine leading to *substitution and it was argued that* N-*chloro intermediates* are unlikely under our experimental conditions. On the basis of a total pH profile from 2 to 12 *it is* abundantly *clear that the attractive* possibility of N-chloro intermediate formation for the fraction of a second cannot be ruled out though such intermediates are not isolable under our conditions. It appears that N-chloro intermediates, formed transitorily in a rate determining step, are rapidly rearranged to halobenzenes till pH 8 and above pH 10 the N-chloro intermediates are rapidly hydrolysed to N-hydroxy compounds which react with an amine molecule in a fast step leading to azobenzenes finally. This report of change over from nuclear halogenation process to a hydrolysis followed by condensation process during an oxidation study over a pH profile is novel and we are the first to report a continuous pH profile in these reactions.

The basis of these suggested changes is as follows :



Step (1) is the halogenation (oxdn.) step, whereas steps (2) and (3) do not involve any oxidation.

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Adsorption of Chlorine by Carbons from Solutions in Carbon Tetrachloride

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Adsorption of chlorine from solution in carbon tetrachloride by carbons, including charcoals, carbon blacks and activated carbons, at 30° is shown to be partly reversible and partly irreversible. The reversible adsorption appears to be dne to surface effects while the irreversible adsorption is found to be due to chemisorption partly in substitution for hydrogen, partly by addition at the unsaturated sites and partly by fixation at some of the active sites constituted by edges, corners and discontinuities on the surface. The irreversibly held chlorine causes a considerable fall in the effective surface area particularly in the case of activated carbons. The carbon-chlorine complex is shown to have a high thermal stability. The data indicate that chlorine is chemisorbed at different sites of varying degrees of energies on placing carbons in contact with chlorine solutionin carbon tetrachloride.

ADSORPTION of chlorine by carbons, including charcoals, carbon blacks and activated carbons, at ambient temperature from aqueous solutions has been reported by Puri et al[1,2] as well as by Rivin and Aron[3] The process involves hydrolysis of chlorine to hydrochloric acid and chemisorption of oxygen in the initial stages (1) and simultaneous chemisorption of both oxygen and chlorine in the later stages (2). Macrae and Oxtoby[4] studied adsorption of ehlorine by coals from non-aqueous solutions at 20° and 60° and found progressive removal of hydrogen from the coals, yielding hydrogen chloride, as well as appreciable chemisorption of chlorine by the coals. The perusal of the literature shows that the interaction of chlorine dissolved in a non-aqueous solvent with carbons other than coals has not been investigated. The use of a non-aqueous solvent avoids the complications caused by the formation of H^+ and Cl^- ions as happens when water is used as the solvent. The effect of chemisorbed chlorine in altering effective surface areas of carbons has also not been looked into so far. The present work was, therefore, undertaken.

Experimental

Materials: Six carbon blacks, two ash-free charcoals prepared by the carbonisation of cane sugar and coconut shells (1) and three commercial activated carbons labelled as B, D and E were used. Their specific surface areas were calculated from adsorption isotherms of carbon dioxide determined at 273°K[5] and surface unsaturation from the amount of bromine adsorbed irreversibly on treatment with aqueous bromine[6]. The hydrogen contents were determined by ultimate analysis. Chlorine was prepared by reacting hydrochloric acid (C.P) with potassium dichromate (C.P.) and purified and dried by the usual methods. It was dissolved in carbon tetrachloride (A. R.) for the reaction.

Procedure: Two portions of carbon (1 g each) were mixed separately with 100 ml chlorine solution of a given concentration in stoppered pyrex-glass bottles wrapped in thick black papers. The suspensions were shaken for a few minutes to effect proper wetting and then allowed to stand with occasional shaking in an incubator maintained at (30°±0.1°) for a required interval of time. The fall in concentration of chlorine, in one case, was estimated by withdrawing an aliquot of the clear supernatant liquid, adding potassium iodide and a known excess of sodium thiosulphate and back titrating against standard iodine solution in the usual way. The amount of HCl formed, if any, was estimated by titrating the same solution against standard sodium hydroxide. To the second suspension as a whole, potassium iodide and a known excess of sodium thiosulphate were added and the mixture allowed to stand in the thermostat for 30 minutes which, in a number of preliminary experiments, was found sufficient to permit 'desorption' of the reversibly adsorbed chlorine. An aliquot was then back titrated against standard iodine. The fall in concentration of chlorine in the first case gave the total amount of chlorine adsorbed while that in the second case gave the amount of chlorine adsorbed irreversibly. The difference between the two gave the amount of chlorine adsorbed reversibly.

Results and Discussion

The total amount of chlorine adsorbed and that of HCl formed on interacting two of the carbons with chlorine solutions of different concentrations for 24 hours are plotted in Figure 1. It is seen that the extent of each reaction increases with rise in concentration of the solution and tends to approach a limiting value as the concentration approaches 0.3 N. The effect of time of contact, using 0.3 N

solution is also shown in the same figure. It appears that 10-12 hrs. contact is sufficient to get the final value in each reaction.

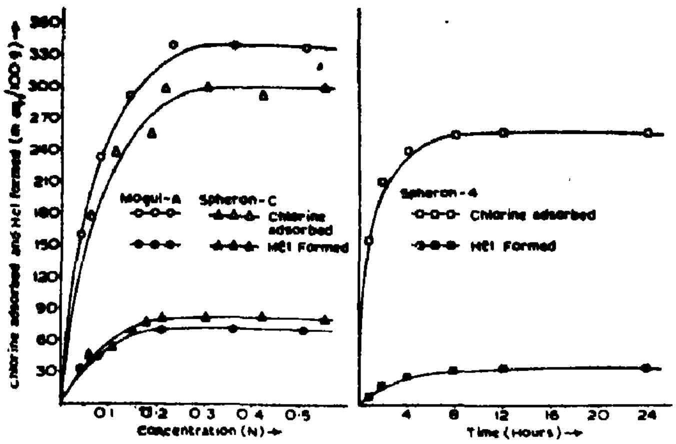


Fig. 1. Effect of concentration of Chlorine and the time of contact on the extent of Chlorine-Carbon reaction.

The formation of HCl in the present experiments cannot be due to hydrolytic adsorption of chlorine as has been observed in the case of interaction with aqueous chlorine[1]. It appears highly probably that HCl is formed through substitution of chlorine for hydrogen, initially present in the carbons, by the reaction

$$\rightarrow C-H+Cl_2 \rightarrow \rightarrow C-Cl+HCl$$

as has been suggested in the case of similar substitution of bromine by previous workers[7]. This indicates possibility of fixation of an equivalent amount of chlorine in substitution for hydrogen in the various carbons.

The amounts of HCl formed and chlorine adsorbed reversibly as well as irreversibly, on keeping various carbons in contact with 0.3*N* solution for 24 hours are given in Table 1. The hydrogen contents, specific surface areas and surface unsaturations are also included in the table. It appears that only a small fraction of the hydrogen can be substituted by chlorine. In this connection it may be noted that Anderson and Emmett[8] as well as Puri and Bansal[9] are of the view that only a small fraction of the combined hydrogen is present on the surface and that the rest of it is dispersed in more than one layer in the interior of the particles.

Physical adsorption of chlorine may by due to surface effects. However, the amount adsorbed could not be related to surface area as the carbons used differed widely in porosity and pore-size distributions. Chemisorption of chlorine is seen to be considerably higher than the HCl formed. It appears that the process involves not only simple substitution but also addition at the unsaturated sites. This view was supported by the observation that surface unsaturation which was appreciable initially (cf. column 4) fell to zero after the interaction. This indicates fixation of an eqnivalent amount of chlorine by the addition process.

In order to get some more insight, two of the carbon blacks as well as sugar and coconut charcoals were outgassed at 600° and 1000° before studying their interaction with chlorine solution in the same manner. The amounts of HCl formed and chlorine chemisorbed are given in Table 2. The values obtained earlier when these carbons had not been outgassed are also reproduced for easy comparison. It is observed that the amount of HCl formed increases as each carbon is outgassed at 600° and decreases as it is outgassed at 1000°. It appears that a part of the hydrogen held within the interior of the particles tends to diffuse out to the surface with increase in kinetic energy of the molecules as the carbons are heated to 600°. This enhances the interaction with chlorine yielding a larger amount of HCl. But when the carbons are evacuated at 1000° very little residual hydrogen is left[10] for reacting with chlorine. The chemisorption of chlorine is seen to rise considerably as the carbons are outgassed. This appears to be due to increase in surface unsaturation (column 3) on elimination of surface oxygen complexes[6].

Considering that a part of the chemisorbed chlorine, equivalent to HCl formed, is fixed in substitution for hydrogen and a part, taken as equivalent to initial surface unsaturation (which

TABLE 1—INTERACTION OF VARIOUS CARBONS WITH CHLORINE DISSOLVED IN CARBON TETRACHLORIDE AT 30°

Sample	Surface area (m^2/g)	Hydrogen content (millieq/100 g)	Surface unsaturation (millieq/100 g)	Amount of HCl formed (millieq/100 g)	Amount of Chlorine (millieq/100 g)	
					Adsorbed physically	Chemisorbed
Philblack-E	182	310	13	20	55	60
Spheron-4	224	478	45	36	81	177
Spheron-6	138 (110)	520	62	28	57	148
Spheron-C	288 (209)	330	70	80	117	183
Mogul-A	252 (176)	510	nil	72	217	123
Mogul	324 (186)	480	nil	48	188	262
Active Carbon B	1005 (309)	2620	155	37	100	680
Active Carbon D	801 (186)	2860	139	63	220	620
Active Carbon E	550 (141)	1940	125	52	74	373
Original Sugar charcoal	338	2940	86	200	104	376
Original coconut charcoal	372	2260	96	72	143	244

TABLE 2—EFFECT OF OUTGASSING CARBON BLACKS AND CHARCOALS ON ADSORPTION OF CHLORINE AND FORMATION OF HCl ON TREATMENT WITH CHLORINE DISSOLVED IN CARBON TETRACHLORIDE AT 30°

Sample	Surface area (m^2/g)	Surface unsaturation (millieq/100 g)	Amount of HCl formed (millieq/100 g)	Amount of Chlorine chemisorbed (millieq/100 g)
Spheron-C				
Original	288	70	80	183
Outgassed at 600°	–	85	108	272
Outgassed at 1000°	–	88	26	149
Mogul-A				
Original	252	nil	72	123
Outgassed at 600°	278	62	100	193
Outgassed at 1000°	182	70	28	164
Sugar Charcoal				
Original	338	86	200	376
Outgassed at 600°	660	376	228	657
Outgassed at 1000°	323	405	nil	488
Coconut shell charcoal				
Original	372	96	72	244
Outgassed at 600°	692	339	92	597
Outgassed at 1000°	423	352	nil	490

TABLE 3—ACCOUNT OF CHLORINE ADSORBED IRREVERSIBLY BY VARIOUS CARBONS

Sample	Total chlorine irreversibly adsorbed (millieq/100 g)	Amount fixed possibly in substitution for hydrogen (millieq/100 g)	Amount fixed possibly by addition at unsaturated sites (millieq/100 g)	Amount of chlorine unaccounted for (millieq/100 g)
(1)	(2)	(3)	(4)	(5)
Philblack E	60	20	13	27
Spheron-4	177	36	45	96
Spheron-6	148	28	62	58
Mogul	252	48	nil	204
Active Carbon B	680	37	155	486
Active Carbon D	620	63	139	418
Active Carbon E	373	52	125	196
Spheron-C				
Original	183	80	70	33
Outgassed at 600°	272	108	85	79
Outgassed at 1000°	149	26	88	35
Mogul-A				
Original	123	72	nil	51
Outgassed at 600°	193	100	62	31
Outgassed at 1000°	164	23	70	71
Sugar charcoal				
Original	376	200	86	90
Outgassed at 600°	657	228	376	53
Outgassed at 1000°	488	nil	405	83
Coconut charcoal				
Original	244	72	96	76
Outgassed at 600°	597	92	339	166
Outgassed at 1000°	490	nil	352	138

falls to zero after the reaction) is fixed by addition at the unsaturated sites, It is observed from the data presented in Table 3 that an appreciable amount of chemisorbed chlorine remains 'unaccounted for' in each case. It appears quite likely that some chlorine is also chemisorbed at certain other active sites, constituted, probably by edges, corners and discontinuities or is entrapped within some of the pores of the adsorbents and requires energy of activation to diffuse out of the system.

The specific surface areas of some of the carbons after chemisorption of chlorine were also determined. These are given in parentheses in Table 1. There is, evidently, an appreciable fall in surface area in each case, particularly so in the case of active carbons which are known to be highly porous. It appears that chemisorbed chlorine occupies a considerable proportion of the internal surface in carbons.

Thermal stability of carbon-chlorine surface

complex resulting from chemisorption of chlorine was checked by determining the amount of chlorine eliminated on outgassing some of the chlorinated carbons at gradually increasing temperatures. It was found that chlorine could be recovered only as HCl, presumably due to combination with the residual hydrogen held by the carbons. The elimination as HCl was found to commence only at 400° (Fig.2) in the case of Spheron-C, which is known to be essentially non-porous, and to stop at 600° even though only 30 milliequivalents out of the total of 272 milliequivalents of chlorine could be thus recovered. The residual chlorine could not come off even on raising the temperature to 1000° in vacuum.

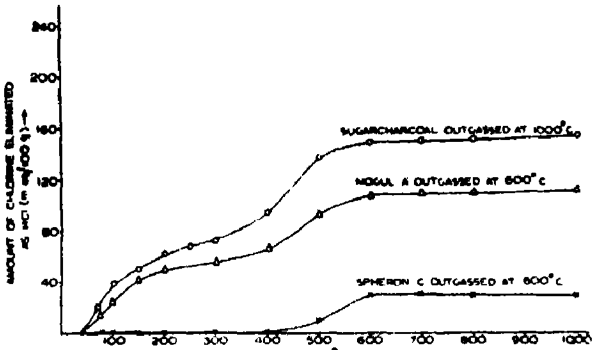


Fig. 2. Elimination of chemisorbed chlorine as HCl on outgassing chlorinated carbons at different temperatures.

The elimination of chlorine as HCl in the case of Mogul-A and sugar charcoal which are known to be porous, however, commenced at a lower temperature, close to 70° and continued thereafter, although the rise in temperature had a gradually decreasing effect, as is evident from the decreasing slope of the graph between 70° and 300°. At 300° there was again a spurt and the elimination proceeded at a relatively faster rate up to 600° beyond which, again, there was a levelling effect up to 1000°. It is observed that only about half of the chlorine chemisorbed by Mogul and less than half of the chlorine chemisorbed by sugar charcoal could be recovered as HCl even on evacuating the systems at 1000°. The rest of the chlorine remained intact even under these rather drastic conditions of desorption.

The data plotted in Figure 2 indicate not only high thermal stability of carbon-chlorine surface complexes formed at ordinary temperatures but also show that chlorine is chemisorbed at different sites of varying degrees of energies on placing carbons in contact with chlorine solution in carbon tetrachloride.

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Studies on the Thermodynamics of Cobalt Exchange on Na-Kaolinite and Na-Illite

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The ion-exchange equilibria of cobalt with Na-kaolinite and Na-illite was studied. The exchange isotherms indicated a lower affinity for cobalt as compared to sodium on both the clays. The affinity varied with temperature. Free energy, enthalpy and entropy generally supported the inferences drawn from the exchange isotherms.

COBALT and other basic cations have been shown by many authors to combine with a variety of soils and soil forming minerals. Their results have been discussed in terms of exchange reactions, complex formation and lattice penetration. The *p*H is one of the dominant factors controlling the distribution of an element into one of these forms. Many equations[1,2] have been proposed to describe the ion exchange processes and measure their quantitative aspects. In this paper an attempt has been made to investigate the equilibrium exchange of sodium and cobalt in two important clay minerals viz., illite and kaolinite at a low *p*H. In view of the great importance of cobalt as a trace element in plant metabolism and animal nutrition it was considered useful to extend our earlier work on the thermodynamics of cobalt exchange to some other clay minerals viz., kaolinite and illite. The basis of the treatment have been the thermodynamic formulations of earlier workers[3,4,5].

Experimental

Both the clays were A.P.I. monomineralic samples. Kaolinite was from Bath, South Carolina and illite from Morris, Illinois, USA. The less than 2u clays were dispersed to sodium forms according to the method of Aldrich and Buchanan[6]. The concentration of the suspensions was adjusted to 1.5% (*w*/*v*) and a *p*H equal to 4 with dil HNO_3. The adjustment to a low *p*H became necessary to prevent hydrolysis, precipitation and hysteresis effects[7]. The CEC of kaolinite and illite at *p*H 4 as determined by the ammonium acetate method were 5.0 and 15.0 meq. per 100 g respectively. The exchanges were carried out at 25 ± 0.1° and 50 ± 0.1° in both the clay minerals as per the method described earlier[8,11]. The suspensions were then centrifuged and cobalt estimated colorimetrically using 1-nitroso-2-naphthol as a colour reagent at 530 mu and sodium by flame photometry. The corresponding concentrations of sodium in the clay phases were obtained by difference (CEC minus concentration of the cation in the supernatant liquids) and that for cobalt from cobalt added minus cobalt in the supernatant liquids.

Evaluation of Thermodynamic Quantities

The reaction between the sodium clays and Co^{2+} can be represented by the equation

$$Na_2^+\text{-clay} + Co^{++} \rightleftharpoons Co^{++}\text{-clay} + 2Na^+ \quad \ldots (1)$$

In terms of equivalent ion concentrations in the clay phases and the solutions the exchanges can be described by the equation[9]

$$\bar{C}_{Na} + C_{Co} \rightleftharpoons C_{Na} + \bar{C}_{Co} \quad \ldots (2)$$

The equivalent ionic fractions of cobalt in the kaolinite and illite phases and in the respective solutions were calculated from the expressions

$$\bar{X}_{Co} = \frac{\bar{C}_{Co}}{\bar{C}}, \quad X_{Co} = \frac{C_{Co}}{C},$$

$$\bar{X}_{Na} = \frac{\bar{C}_{Na}}{\bar{C}} \text{ and } X_{Na} = \frac{C_{Na}}{C} \quad \ldots (3)$$

In the dilute range of concentration studied by us the selectivity coefficients were (taking the ratio of activity coefficients as unity[10]) calculated from the equation

$$K_C = \frac{\bar{X}_{Co}(X_{Na})^2}{(\bar{X}_{Na})^2 X_{Co}} \quad \ldots (4)$$

and the thermodynamic equilibrium constant K from the equation[11]

$$ln\, K = (Z_A - Z_B) + \int_0^1 ln\, K_C d\, \bar{X}_{Co} \quad \ldots (5)$$

The thermodynamic functions ($\Delta G°$, $\Delta H°$ and $\Delta S°$) were then calculated by utilising the van't Hoff reaction isotherm for $\Delta G°$, the van't Hoff isochore for $\Delta H°$ and the Gibbs-Helmhotz equation for $\Delta S°$[12]. The values are given in Table 1.

TABLE—1 THERMODYNAMIC VALUES FOR COBALT EXCHANGE WITH Na-KAOLINITE AND Na-ILLITE AT 25° AND 50°

Thermodynamic parameters	Exchange in kaolinite 25°	Exchange in kaolinite 50°	Exchange in illite 25°	Exchange in illite 50°
K	0.188	0.242	0.111	0.100
ΔG° (cal/mole)	990.3	912.6	1304.6	1488.7
ΔH° (cal/mole)	1915.5		−761.2	
ΔS° (cal/mole)	3.1	3.1	−6.9	−6.9

Results and Discussion

From the values of equivalent ionic fractions at 25° and 50° calculated for cobalt exchanges in Na-kaolinite and Na-illite vide expressions in eqn. 3, exchange isotherms were plotted and are given in Figure 1. The isotherms were of Lang-

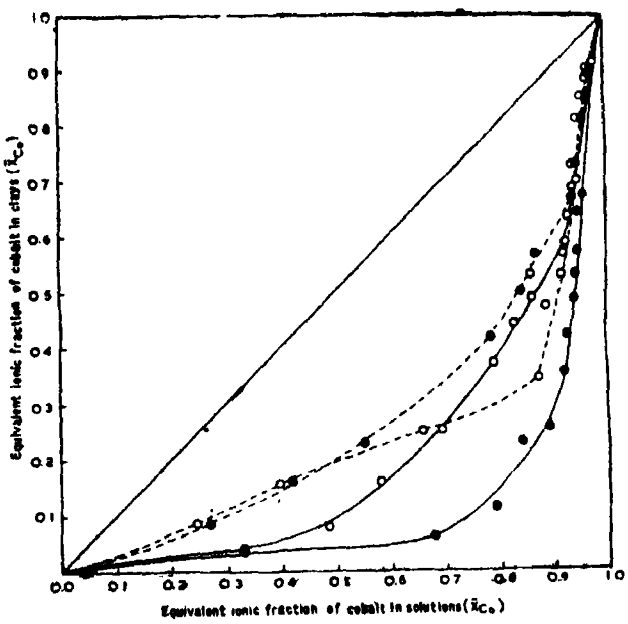


Fig. 1. Exchange isotherms of Cobalt on Sodium-kaolinite and Sodium-illite at different temperatures.
—O— Kaolinite (25°)
—●— Kaolinite (50°)
—O— Illite (25°)
—●— Illite (50°)

muir type and their deviation from the diagonal indicated a strong preference for sodium as compared to cobalt both by kaolinite as well as illite. An examination of the isotherms further revealed that the affinity of cobalt for Na-kaolinite was greater than for Na-illite. Further the affinity was affected by temperature, being higher at 50° as compared to 25° in kaolinite and in a reverse order in illite.

Values of selectivity quotients (Kc) were calculated vide eqn. 4. Plots of log Kc against equivalent ionic fractions of cobalt are given in Figure 2. Using the trapezoidal rule the areas under these curves were utilised for calculating the values of equilibrium constants for the reactions in kaolinite and illite at 25° and 50° and are given in Table 1. In the exchange in Na-kaolinite the value

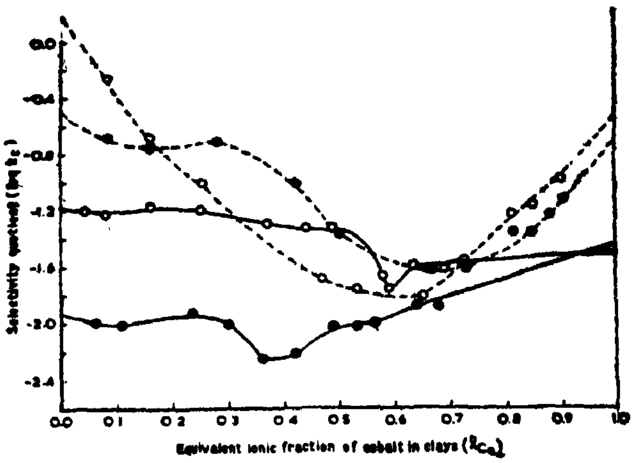


Fig. 2. Logarithms of Selectivity Quotients vs. Equivalent ionic fractions of Cobalt in kaolinite and illite,
—O— Kaolinite (25°)
—●— Kaolinite (50°)
—O— Illite (25°)
—●— Illite (50°)

of the equilibrium constant at 50° was higher than 25° indicating a higher preference for cobalt as compared to sodium in kaolinite at the high temperature. The values followed a reverse order at the two temperatures in illite. The results were in accordance with the deductions drawn from the exchange isotherms.

An examination of Table 1 further revealed that the free energy changes (ΔG°) during the reactions were positive. These were indicative of a non-spontaneity of exchange in the direction of cobalt in both the clays. The difference in the values of free energy changes at 25° and 50° was much greater in the case of exchange on illite than in the case of kaolinite. The enthalpy changes (ΔH°) were in accordance with temperature dependant exchanges, the reaction being endothermic during cobalt exchange on Na-kaolinite and exothermic during its exchange on Na-illite. Thus cobalt was more strongly bound on illite and less strongly bound on kaolinite in comparison to sodium. The release of cobalt in illitic sodic soil process may not. therefore, be so easy as in the case of kaolinitic sodic soils. These results found support from entropy changes during the exchanges. Thus the greater disorder indicated by positive entropy effects during cobalt exchange on Na-kaolinite was in accordance with the low strength of binding of cobalt on kaolinite as a result of an extended diffuse distribution of cobalt ions in the electrical double layer. On the other hand, negative entropy changes during cobalt exchange on Na-illite were in accordance with a greater strength of binding of cobalt to fixed specific sites on the illite surface producing a greater order in the system.

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Linear Free-Energy Relationship in Mixed Solvents

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The nature of the variations of ρ with solvent systems has been explored. The change in ρ-values cannot be explained on the basis of electrostatic theory. The changes in ρ- and σ-values have been tried to be correlated with changes in field and mesomeric effects.

THE role of solvents on the dissociation constants of weak acids has not been well-understood. It has been well established that solute-solvent interactions of uncertain magnitude have a profound effect on the dissociation constants which could not be well explained on the basis of simple electrostatic theory.

Little attempt, however, has been made to elucidate the role of solvents on the Hammett's reaction parameter ρ. The ρ-value is dependant on the reaction, nature of the solvent system and temperature[1,2] Thus, the change of the solvent should have a profound effect on ρ.

In order to elucidate the effect of solvents on ρ, we determined the dissociation constants of benzoic acid, *m*-chloro, *m*-fluoro, *p*-bromo and *p*-iodo benzoic acids in ethanol-water and methanol-water mixtures by the modified conductometric method suggested by Gelb[3] and also by Fuoss-Kraus method[4]. Since σ-values are generally assumed to be independent of solvent, the pK-values of benzoic acids in methanol+water and ethanol+water mixtures should be a linear function of the corresponding pK-values of benzoic acids in water.

The Hammett equation in water (W) and other solvents (S) can be represented as :

$$pK_A(W) = pK_{A_0}(W) - \rho_w \sigma \quad \cdots \quad (1)$$

and

$$pK_A(S) = pK_{A_0}(S) - \rho_s \sigma \quad \cdots \quad (2)$$

A = Substituted acid,

A_0 = Unsubstituted acid.

Thus, we have,

$$pK_A(S) = (\rho_s/\rho_w)\, pK_A(W) + [pK_{A_0}(S) - (\rho_s/\rho_w) pK_{A_0}(W)] \quad \cdots \quad (3)$$

for the relationship $pK_A(S)$ and $pK_A(W)$. Thus, from the plots of $pK_A(S)$ against $pK_A(W)$ should give straight lines[5] from the slope of which ρ_s/ρ_w, thus ρ_s could be calculated since $\rho_w = 1$. This can also be obtained from the relationship (2).

With the limited data available, we are able to find ρ_s-values in different mixed solvents. The ρ_s-values show maximum in the region 60-80 wt% of organic solvents (Table 1) similar to the observations of Rochester[5] and others[6].

TABLE—1

Wt % of MeOH	8.0	16.0	25.0	34.4	44.7	54.2	64.1	75.9	
	1.01	0.92	0.99	1.10	1.16	1.27	1.55	1.25	
Wt % of EtOH	8.0	16.4	25.3	34.4	44.0	54.1	64.7	76.0	87.6
	0.80	0.73	0.90	0.94	1.10	1.18	1.33	1.11	0.88

ρ-values have been observed to be consistently more positive in methanol-water than in ethanol-water mixtures. At low percentages of the organic solvents ρ is less than 1 and becomes more than 1 near about 0.1 mole-fraction of organic solvent. This can probably be correlated with the significant structural and consequent entropy changes in the medium around 0.1 mole-fraction of alcohol[7]. It is known that an enhancement of solvent structure occurs and becomes maximum around $X_s = 0.1$ of alcohol[8]. The increasing positive value of ρ in mixed solvents indicates the greater facilities for the development of partial negative charge on the side-chain[9] which is more pronounced in methanol-water than the corresponding ethanol-water mixtures. This must be related to medium effects as everything is common except the solvent systems.

For the reaction :

$$HA_0 + A^- \rightleftharpoons HA + A^-_0 \quad \cdots \quad (4)$$

We have,

$$pK = \rho\sigma = \frac{\Delta G_{nonel}}{2.303\,RT} + \frac{\Delta G_{el}}{2.303\,RT}$$

$$= \frac{\Delta G_{nonel}}{2.303\,RT} + \frac{Ne^2}{2 \times 2.303\,RT\epsilon}\left(\frac{1}{\gamma_{A_0^-}} - \frac{1}{\gamma_{A^-}}\right) \quad \cdots \quad (5)$$

Thus, a linear relationship of ρ against $\frac{1}{\epsilon}$ is expected. But the relationship fails in mixed solvents. This

is quite natural due to the approximate nature of the Born equation[10] where the dielectric constant have been regarded to be the macroscopic dielectric constant. Polarization of the solvent molecules by ions and consequent changes of the dielectric constant have been neglected altogether. No theoretical equation, however, exists to account for the variations of the dielectric constant with radii of ions though the dielectric constant is known to be a function of radii of ions[11]. The equations [12,13] which account for the variations in dielectric constant with distance are purely empirical and inadequate. Even the theory of Hiromi[14] which takes into account the particular geometry and charge distribution with organic ion is inadequate as the equation also predicts the variation of pK with $1/\epsilon$. It is, however, known that the dielectric constant is not the only property which determines the variations in pK but medium effects, i.e., solute-solvent interactions, solvent-basicity and solvent-structure, etc., are of importance to know the nature of the variations of ρ with solvent systems.

The failure of the relationship may be partly due to changed values of σ in mixed solvents due to change in medium effects. σ is known to change with solvent as evident from the works of Bright and Briscoe[15] and others[2,16]. This is also apparent from theoretical point of view as explained by Dewar and Grisdale[17] :

σ is dependant on (1) direct electrostatic (or field) effect and (2) mesomeric effect, i.e.,

$$\sigma^{-} = F/\gamma_{i,j} - M\pi_{i,j} \qquad .. \quad (6)$$

F and M are constants determining the field and resonance effect, $\pi_{i,j}$ and $\gamma_{i,j}$ are the atom-atom polarizability of the aromatic system and the distance between the points of attachment to the aromatic system of the substituent and side-chain respectively.

Inspite of the limitations of the equations, it has been successfully utilised by Dewar and Grisdale[17].

No theoretical treatment of evaluation of ρ-values has been made. It is reasonable to believe that the field and mesomeric effects and the complex interactions the reactants undergo in solution should be responsible for the change in ρ-values.

The direct electrostatic effect is dependant, besides other factors, on the effective dielectric constant[18] which definitely changes with change in the solvent systems leading to a change in the σ-values, mesomeric effect probably will have little effect in changing σ-values in mixed solvent. However, It is not definite as to what extent the dielectric constant affects the σ-values.

A correlation of ρ-values calculated from pK values of well-behaved meta-substituted compounds with γ-values has been made by Grunwald et al[19], σ-values are regarded to be independent of solvents in his treatment also.

It is thus apparent that unambiguous method for the evaluation of ρ- and σ-values in mixed solvents as well as more data are needed before any correlation of ρ-values with γ- or any other solvent parameter could be made.

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Conductance of Cesium Halides, Rubidium Nitrate and Rubidium Iodide in Diethyleneglycol and Aqueous Diethyleneglycol at 25°

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Conductance measurements on cesium halides, rubidium nitrate and rubidium iodide in diethyleneglycol (DEG) and aqueous diethyleneglycol (aq. DEG, 20% by weight) have been carried out at 25°. Experimental data have been analysed for limiting equivalent conductances at infinite dilution, Λ_0, and Walden products, $\Lambda_0\eta_0$, on the basis of Onsager's equation and Owen's method. Walden products, mobilities and solvation numbers of the single ions in these solutions have been estimated. Results have been further discussed in terms of the ion-solvent interaction.

A substantial body of data on the conductances of ions in many non-aqueous solvents like HMPA[1,2], propylene carbonate[3,4] and trifluoroethanol[5], sulfolane[6], DMSO[7], DMF[8] and acetone[9], etc.; and aqueous mixtures of methanol[10,11], propylene carbonate[11] and ethyleneglycol[12], etc., have recently been reported. But no study on conductance of electrolytes in DEG and its aqueous mixtures is reported in the literature, although DEG has figured in the literature as a solvent in which reaction kinetics has been investigated over a wide range of temperature and a study[13,14] concerning oxidation-reduction potential of the iodine-iodine system is reported. The present study has, therefore, been carried out to collect the data on conductance of 1 : 1 electrolytes in DEG, and to get the information regarding ion-solvent interactions from the mobilities and Walden products of the ions in the solvent. The determination of single ion conductivities in non-aqueous solvents has been hampered by experimental difficulties encountered in the application of standard methods of obtaining transport numbers[15]. This has, therefore, led to the use of various empirical methods to determine the single ion conductivities, which are based upon the assumption of equal mobilities of ions of certain reference electrolytes such as tetraisoamyl-ammonium tetraisoamyl-boride[16,17]. But in the present study, Stoke's assumption[18] of relating Walden product, $\Lambda_0\eta_0$, with radii of the halide ions has been employed to estimate the single ion mobilities, Walden products and solvation numbers in diethyleneglycol.

Experimental

Diethyleneglycol (VEB lab., Germany) was purified by fractional distillation under reduced pressure. It was further purified by fractional crystallization by partial freezing. The purified diethyleneglycol (DEG) had the following physical constants at 25° : Density, $d_0 = 1.11478$ g.cm^{-3}, viscosity, $\eta_0 = 0.0174$N.s.m^{-2}, and specific conductance, $\kappa = 5\times10^{-7}$ S.cm^{-1}. The values for the density and specific conductance of the purified sample are in agreement with the literature[19] values within the experimental error. However, the value for the viscosity is markedly low. The extraordinary high value of viscosity reported in the earlier studies[19] may be due to the presence of higher glycols in their sample.

Water used for the preparation of aqueous mixture of diethyleneglycol (20 per cent. by weight) was purified by triple distillation over alkaline $KMnO_4$. It had a specific conductance of 1.3×10^{-6} S.cm^{-1}.

Cesium chloride, bromide and iodide and rubidium nitrate and iodide were of Analar grade and were crystallised from water, dried and stored over P_2O_5 in a vacuum desiccator.

All solutions were made by weight under dry conditions, Conversion between equivalent concentration and molality was obtained from the usual relationship[20]. Measurements on conductance were carried out in the manner similar to that reported in our earlier publications[21-24].

Results and Discussion

The equivalent conductance values of CsCl, CsBr, CsI, $RbNO_3$ and RbI in DEG and aq. DEG at 25° are given in Table 1.

TABLE—1 EQUIVALENT CONDUCTANCE OF CsCl, CsBr, CsI, $RbNO_3$ AND RbI IN DEG AND AQ. DEG AT 25°

DEG		Aq. DEG (20%, by weight)	
C × 10^4 (mol. l^{-1})	Λ_{obs} (S. cm^2.mol^{-1})	C × 10^4 (mol. l^{-1})	Λ_{obs} (S. cm^2.mol^{-1})
CsCl		*CsCl*	
13.72	4.45	46.52	92.64
36.53	4.38	68.57	90.52
54.21	4.32	85.70	88.76
87.67	4.24	108.27	86.50
100.54	4.21	127.56	84.22
		163.53	83.20
CsBr		*CsBr*	
40.62	4.00	48.60	90.52
60.21	3.90	60.10	88.72
74.94	3.78	72.50	87.80
97.06	3.70	86.32	86.80
111.32	3.65	108.39	85.00
		135.14	83.40
CsI		*CsI*	
50.16	3.96	30.72	87.80
63.78	3.92	42.66	86.10
75.18	3.87	62.75	84.20
86.48	3.85	72.83	82.25
96.80	3.83	89.24	80.72
		108.85	78.50
		127.84	77.80
RbI		*RbI*	
12.00	3.92	38.56	89.75
28.92	3.84	45.26	87.20
39.71	3.80	63.25	84.68
48.66	3.75	78.24	82.50
59.64	3.70	98.62	80.08
74.79	3.65	125.94	78.64
$RbNO_3$		*$RbNO_3$*	
25.74	3.78	40.05	90.88
45.69	3.68	56.11	87.68
56.55	3.62	70.37	82.85
73.38	3.58	83.56	80.00
88.59	3.52	93.67	78.54
104.12	3.48	121.50	76.50

A precise estimate of Λ_0 for these electrolytes in DEG and Aq. DEG is obtained by a method proposed by Owen[25]. This is based on the conductance equation :

$$\Lambda = \Lambda_0 - SC^{\frac{1}{2}} + AC \log C + BC \quad \dots (1)$$

where S refers to the limiting Onsager slope, A and B are the constants.

For extrapolation purposes, equation (1) is written as :

$$\frac{\Lambda + SC^{\frac{1}{2}} - \Lambda_0}{C} = A \log C + B \quad \dots (2)$$

So that when the left-hand side is plotted against log C, a straight line will result if the correct value of Λ_0 has been chosen. This choice is made by trial and error. The values of Λ_0 for salts in DEG and aq. DEG, which gave the best straight lines according to relation (2), are given in Table 2, alongwith the values obtained according to Onsager's equations[26]. Using, Λ_0, as estimated from Owen's method, Walden products, $\Lambda_0\eta_0$, for the electrolytes in DEG and Aq. DEG have also been estimated and they are included in the Table 2, alongwith the Λ_0 values.

TABLE—2 VALUES OF Λ_0, $\Lambda_0\eta_0$, FOR CsCl, CsBr, CsI, RbI AND $RbNO_3$ OBTAINED FROM ONSAGER'S AND OWEN'S EQUATIONS IN DEG AND AQ. DEG (20 PER CENT. BY WEIGHT) AT 25°.

Electrolyte	Λ_0 (Ons.) (S. cm^2.mol^{-1})	Λ_0 (Owen) (S. cm^2. mol^{-1})	$\Lambda_0\eta_0$ (S. mol^{-1}.N.S.10^{-3})
DEG			
CsCl	4.62	4.55	0.79
CsBr	4.66	4.45	0.77
CsI	4.20	4.30	0.74
RbI	4.15	4.05	0.70
$RbNO_3$	4.05	4.15	0.72
Aq. DEG (20 per cent., by weight)			
CsCl	103.00	107.00	1.68
CsBr	100.00	105.00	1.65
CsI	97.50	98.00	1.54
RbI	104.00	103.00	1.62
$RbNO_3$	111.60	112.00	1.76

Now according to Walden[27], the product, $\Lambda_0\eta_0$, given in the last column of Table 2 should be constant for each salt. But, it is not found to be so in the present study. However, the loss of ionic mobilities does not parallel the change of viscosity of the solvent, and these variations may be related to structural modifications[28].

The Walden product may be given by the equation[26] (3) :

$$\Lambda_0\eta_0 = (\lambda_0^+ + \lambda_0^-)\,\eta_0 = \frac{\epsilon F}{6\pi}\left(\frac{1}{r^+} + \frac{1}{r^-}\right) \quad \dots (3)$$

where ϵ is the charge on the ion, F is the force acting on a particle, r^+ and r^- are the radii of the cation and anion respectively.

Walden products, $\lambda_0^+\eta_0$ and $\lambda_0^-\eta_0$ for the individual ions and hence the single ion mobilities in DEG and Aq. DEG were, therefore estimated by plotting $\Lambda_0\eta_0$ versus the inverse of the radii of the halide ions, $\frac{1}{r_-}$. Linear relations were found to exist both in DEG as well as in Aq. DEG solutions of CsCl, CsBr, and CsI. By extrapolating the straight lines to $\frac{1}{r_-} = 0$, $\lambda_0^+\eta_0$ for the cation (Cs^+ in the present case) was estimated in DEG and Aq. DEG from their respective plots. Then on substracting the value of $\lambda_0^+\eta_0$ for Cs^+ ion thus estimated from the values of $\Lambda_0\eta_0$ for the electrolytes (viz. CsCl, CsBr and CsI, given in Table 2), the values of $\lambda_0^-\eta_0$ for Cl^-, Br^- and I^- ions in DEG were evaluated. On substracting $\Lambda_0\eta_0$ of RbI from $\lambda_0^-\eta_0$ for I^- ion, $\lambda_0^+\eta_0$ for Rb^+ ion was estimated and subsequently the value of $\lambda_0^-\eta_0$ for NO_3^- ion was known. The same procedure was applied to estimate the ionic Walden products in Aq. DEG. And, then on dividing the

respective ionic Walden products by the viscosity of the solvent, mobilities of the each ion, was also estimated in DEG and in Aq. DEG respectively.

The values of $\lambda_0^+\eta_0$ and $\lambda_0^-\eta_0$, alongwith values of λ_0^+ and λ_0^- for Cs^+. Rb^+ and Cl^-, Br^-, I^- ions in DEG and Aq. DEG respectively are given in Table 3.

TABLE—3 IONIC WALDEN PRODUCTS AND MOBILITIES IN DEG AND AQ. DEG

Ion	$\lambda_0^+\eta_0$ (S.mol.$^{-1}$. N.S.10^{-5})	$\lambda_0^-\eta_0$ (S.mol^{-1}. N.S.10^{-6})	λ_0^+ (S.cm^2. mol^{-1})	λ_0^- (S.cm^2. mol^{-1})
		DEG		
Cs^+	0.52	–	2.99	–
Rb^+	0.48	–	2.76	–
Cl^-	–	0.27	–	1.55
Br	–	0.25	–	1.44
I^-	–	0.22	–	1.26
NO_3^-	–	0.24	–	1.38
		AQ. DEG (20 PER CENT., BY WEIGHT)		
Cs^+	0.83	–	52.87	–
Rb^+	0.85	–	54.14	–
Cl^-	–	0.85	–	54.14
Br^-	–	0.82	–	52.28
I^-	–	0.71	–	45.22
NO_3^-	–	0.91	–	57.96

Table 3 shows that the limiting equivalent conductances and the Walden products for both the cations (Cs^+ and Rb^+) and all the anions (Cl^-, Br^-, I^- and NO_3^-) have greater magnitudes in Aq. DEG than in DEG. This may be attributed to the greater structure of DEG-H_2O than DEG. Since the structure breaking ions viz. Cl^-, Br^-, I^-, Rb^+ and Cs^+ will then break more structure in Aq. DEG than in DEG. The resulting decrease in viscosity is greater in the case of Aq. DEG than DEG and, therefore, it could produce the increase in the conductance-solvent viscosity product (i.e., Walden product) for these ions in Aq.DEG over that in DEG. In other words, greater mobilities of the ions in Aq. DEG than in DEG may be interpreted as a measure of lesser ion-solvent interaction in the former case. These conclusions agree with those deduced from greater positive B-values obtained from the viscosity data[29] in case of Aq. DEG.

Table 3, therefore, suggests that the following order of ion-solvent interaction exists in DEG :

$$Cl^- > Br^- > NO_3^- > I^- \; ; \; Cs^+ > Rb^+$$

whereas in Aq. DEG, following is the order of ion-solvent interaction :

$$NO_3^- > Cl^- > Br^- > I^- \; ; \; Rb^+ > Cs^+$$

Solvation numbers for the ions in DEG were also estimated from their respective mobilities (Table 3) using the Stoke's[18] relation, according to which the ionic solvated volume should be obtained, because of the packing effects from the equation (4) :

$$V_s^0 = 4.35\, r_s^3 \qquad \ldots (4)$$

where V_s^0 is the ionic solvated volume and is expressed in mol/mole and r_s is the radii of the solvated ions in angstroms. The solvation number, n_s, was obtained from the relationship[30] :

$$n_s = \frac{V_s^0}{\bar{V}_0} \qquad \ldots (5)$$

where $\bar{V}_0$ is the molar volume of the solvent (DEG in the present study). The radii, r_s, of the ions viz., Cl^-, Br^-, I^-, Cs^+, Rb^+ and NO_3^- ions used to calculate V_s^0 (from equation 5) were taken as the Paulings[31] radii. The solvation numbers of the ions in DEG thus estimated from equation (5) are given in Table 4.

TABLE—4 SOLVATION NUMBERS OF THE IONS IN DEG FROM THE MOBILITY METHOD

Ion	Solvation Number n_s
Cs^+	0.25
Rb^+	0.17
Cl^-	0.31
Br^-	0.39
I^-	0.53
NO_3^-	0.29

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Viscosity and Molecular Interaction in Binary Mixtures of Some Polar and Nonpolar Liquids with Dimethylsulphoxide

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Viscosities of some polar and non-polar liquids in admixture with DMSO have been measured at 30° and 40° and the results have been examined in the light of the relations developed for binary mixtures. The value of the interaction energy 'W' is calculated for each of the mixture at 30°,

VISCOSITY data of binary liquid mixtures have been employed to yield information regarding the nature of interaction[1,2] in solution. In continuation with our work on molecular interaction in liquid mixture, it was considered desirable to undertake viscosity measurements of binary liquid mixtures of some non-polar liquids, e.g.. Benzene, Dioxane, Toluene, and polar like Chlorobenzenes and Nitrobenzene liquids with DMSO. Literature reveals that very little attention seems to have been paid[3-5] to determine the viscosity of binary liquid mixtures containing DMSO as one of the components. Our excess volume of mixing[6] measurement have shown dipole-dipole and dipole-induced dipole interactions between the components. The results of viscosity measurements have been analysed on the basis of the relations developed by Katti and Chaudhari[7] and adopted by Raman, Naidu and Krishnan[8], for non-ideal solutions.

Materials and Methods

DMSO and other liquids were purified and purity was checked as reported earlier.[6]

Viscosity of mixtures was determined with a modified Ubbelohde viscometer having appropriate auxiliary equipment to keep off atmospheric moisture from the system as far as possible. The accuracy of the viscometer was checked by measuring viscosities of pure Benzene and Chlorobenzene. The agreement with the corresponding literature values appears to be quite good.

Mixtures of known compositions were prepared by weight, precaution being taken to keep the solvent and solution out of contact with atmosphere as far as possible. The mixture was transferred to the viscometer which was then suspended in a water thermostat controlled to ±0.01°. The time of flow of the liquid through capillary was noted. Density of the mixture was also determined side by side with a caped dilatometer. For each system measurements were made at 30° and 40° and the viscosity was then obtained from density and time of flow data in the usual manner.

Results and Discussion

The viscosity of mixtures (η_s) was found to decrease with the increase in temperature. Except the DMSO+Nitrobenzene system, all mixtures deviate negatively from the mixture law, i.e., the viscosity of the mixture is less than expected from mixture law. For DMSO+Nitrobenzene system, η_s-values show almost an ideal behaviour at 30° and 40°.

In order to substantiate the above finding, the data were examined in the light of conclusions drawn by Fort and Moore[8], by calculating excess viscosity of mixing, η^E represented by

$$\eta^E = \eta_S - (\eta_A X_A + \eta_B X_B)$$

where η_S is the viscosity of the mixture, η_A, η_B are the viscosities and X_A, X_B are the mole fractions of components A and B respectively. The values of η^E so obtained for different systems are given in Table 1.

In another approach to describe the viscosity of binary mixtures, Grunberg and Nissan[9] suggested

$$\ln \eta_{mix} = X_A \ln \eta_A + X_B \ln \eta_B + X_A X_B d$$

where d is proportional to W/RT and W being the interchange energy. The parameter has the same significance as given by Guggenheim[10] in the treatment of his regular solution theory and d has been regarded as a better measure of the strength of interaction between the components in solution. The values of d obtained are also given in Table 1.

It may be noted from Table 1 that except for DMSO+nitrobenzene, all mixtures have negative values of η^E over the entire concentration range. In DMSO+Nitrobenzene system, there is no measurable viscosity change of mixing showing that the system behaves ideally.

TABLE—1 EXCESS VISCOSITY (η^E) AND FACTOR 'd' OF MIXTURES OF DMSO(B) WITH DIFFERENT LIQUIDS (A)

Mole fraction X_A	30°		40°	
	η^E	d	η^E	d
	DMSO(B)+Benzene (A)			
0.2	−0.161	−0.172	−0.110	−0.057
0.3	−0.207	−0.207	−0.147	−0.087
0.4	−0.218	−0.230	−0.182	−0.191
0.5	−0.232	−0.350	−0.165	−0.110
0.6	−0.217	−0.278	−0.149	−0.105
0.7	−0.175	−0.263	−0.124	−0.098
0.8	−0.128	−0.273	−0.089	−0.100
	DMSO(B)+Toluene (A)			
0.2	−0.073	+0.273	−0.105	+0.001
0.3	−0.077	+0.350	−0.115	+0.093
0.4	−0.093	+0.345	−0.112	+0.162
0.5	−0.088	+0.469	−0.099	+0.235
0.6	−0.071	+0.477	−0.095	+0.229
0.7	−0.055	+0.537	−0.042	+0.505
0.8	−0.039	+0.604	−0.019	+0.639
	DMSO(B)+Chlorobenzene (A)			
0.2	−0.105	−0.092	−0.074	−0.066
0.3	−0.138	−0.116	−0.099	−0.031
0.4	−0.154	−0.126	−0.113	−0.099
0.5	−0.172	0.193	−0.118	−0.118
0.6	−0.138	−0.237	−0.122	−0.188
0.7	−0.151	0.291	0.107	−0.218
0.8	−0.127	−0.433	−0.085	−0.318
	DMSO(B)+Nitrobenzene (A)			
0.2	+0.002	+0.001	0.001	−0.011
0.3	+0.002	0.004	0.000	−0.009
0.4	+0.004	−0.002	−0.001	−0.004
0.5	0.000	0.005	−0.003	−0.007
0.6	+0.004	+0.002	0.000	−0.001
0.7	+0.003	+0.004	0.000	−0.028
0.8	+0.002	−0.006	−0.001	−0.053
	DMSO(B)+Dioxane (A)			
0.2	−0.111	−0.332	−0.099	−0.345
0.3	−0.149	−0.364	−0.096	−0.234
0.4	−0.162	−0.364	−0.100	−0.214
0.5	−0.169	−0.384	−0.116	−0.271
0.6	−0.151	−0.366	−0.111	−0.291
0.7	−0.132	−0.390	−0.090	−0.276
0.8	−0.103	−0.422	−0.068	−0.332

The data of d shows that for DMSO+Benzene, DMSO+Chlorobenzene and DMSO+Dioxane, the d-values are negative at both the temperatures over the entire concentration range; d-values generally become less negative with rise in temperature. For DMSO+Toluene, the values of d are positive. The negative values of d and η^E in the mixtures of DMSO with Benzene, Dioxane and Chlorobenzene shows a somewhat weaker interaction. Nigam and Mahl[11] discussed the sign of η^E and d in terms of complex formation between the components. It would be unreasonable to expect complexing in our systems. Perhaps, difference in the size of molecules may also be important in deciding the sign of η^E and d.

Another approach to study molecular interaction in binary liquid mixtures with the help of viscosity data is that of Katti and Chaudhary[7] and Raman et al[8] using Eyring concept of viscosity, they obtained the expression, viz.

$$ln\,\eta_s V_s = X_A ln\,\eta_A V_A + X_B ln\,\eta_B V_B + X_A X_B \frac{W}{RT}$$

where W is the energy of viscous flow. This approach, perhaps would give a more direct idea about the type and extent of interaction between the components. The values of W at 0.5 mole fraction concentration, are given in Table 2.

TABLE—2 VALUES OF 'W' AT EQUIMOLAR CONCENTRATION AT 30°

System	*W in cals./mole*
DMSO+Benzene	−245.8
DMSO+Toluene	+234.6
DMSO+Chlorobenzene	+ 39.1
DMSO+Nitrobenzene	+368.6
DMSO+Dioxane	−279.4

Large negative values of W in DMSO+Benzene and DMSO+Dioxane systems show an appreciable dipole-induced dipole interaction between the components. Appreciable interaction in these systems is also shown by negative values of excess volume of mixing[6]. Positive values of W in DMSO+Toluene, DMSO+Chlorobenzene and DMSO+Nitrobenzene shows weak dipole-dipole interaction between the components as supported by our positive values of V_m^E in these systems[6].

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An Equation for Variation of Viscosity with Temperature

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A modified equation representing the variation of viscosity with temperature over high as well as low temperature regions has been suggested. Calculations have been done for Aniline and Chlorobenzene.

BATCHINSKI[1] and Hildebrand[2] suggested a linear relationship between fluidity ϕ and molar volume V in the form $\phi = B(V - V_0)/V_0$, where V_0 is the molar volume at which viscous flow ceases and B is a constant. Eicher and Zwolenski[3] and later Ertl and Dullien[4] pointed out that while this equation is satisfactory in the 'high' temperature region, at 'low' temperature, i.e., for $T/T_c \leqslant 0.46$ (T_c being the critical temperature), is larger than that predicted by the linear relation, The viscosity data in the low temperature region may be represented by a polynomial relationship between viscosity and molar volume, but such an equation will not hold in the high temperature region.

In the present attempt a semi-empirical equation has been obtained by adding a suitable 'correction' term to the commonly used linear relation and may be written as

$$\phi = z + K\,e^{-x}\,z^n \qquad \ldots \quad (1)$$

where

$$c_1 x = c_1 x + c_2 \qquad \ldots \quad (2)$$

Here x represents $(V - V_0)$, where V is the molar volume at the given temperature and V_0 is the molar volume at the freezing point, which is calculated using the extrapolated value of density. The constants c_1, c_2, K and n are characteristic of the liquid chosen. The correction term $(K\,e^{-x}\,z^n)$ may be regarded as correlated to the 'pre-freezing' effect discussed by Ubbelohde and co-workers[5] and is found to become significant at low temperature and negligible in the high temperature region.

The constants c_1 and c_2 in eq. (1) may be determined by using standard linear regression technique taking the viscosity data in the high temperature region only and assuming that the correction term is negligible in this region. This assumption is justified by the results obtained in the end. In order to determine the remaining two constants K and n, we write eq. (1) as

$$[\ln(\phi - z) + x] = n(\ln z) - \ln K \qquad \ldots \quad (3)$$

and perform linear regression calculations using the new variables and making use of the data in the low temperature region. Calculations were done for the two liquids Chlorobenzene and Aniline, whose viscosity[6,7,9] and density[8] data are easily available in the low as well as high temperature regions. For making least square fit, the boundary between the two regions was taken at 0° for Chlorobenzene and at 40° for Aniline. This choice is, however, relevant to the available data only and is by no means unique. The values of constants determined in this way are given in Table 1, which also lists the freezing points aud the V_0 values.

TABLE—1

System	c_1	c_2	K	n	Freezing point(°C)	V_0(cm³/mol)
Chlorobenzene	0.165	0.242	1.012	1.500	−45.2	89.187
Aniline	0.151	0.119	0.373	0.066	− 6.1	95.604

TABLE 2

COMPARISON OF EXPERIMENTAL AND CALCULATED VALUES OF FLUIDITY, (CP^{-1})

Chlorobenzene[6,9]			Aniline[7]		
Temp.	Experimental	Calculated	Temp.	Experimental	Calculated
−45	0.376	0.362	5	0.124	0.122
−41	0.421	0.419	10	0.153	0.156
−38	0.454	0.457	15	0.188	0.187
−34	0.501	0.504	20	0.227	0.225
−30	0.546	0.551	25	0.269	0.269
−26	0.600	0.598	30	0.316	0.318
−20	0.685	0.672	35	0.369	0.370
−10	0.801	0.808	40	0.422	0.422
0	0.950	0.947	50	0.540	0.542
4.7	1.012	1.017	60	0.662	0.665
9.7	1.091	1.093	70	0.787	0.791
15.9	1.179	1.190	80	0.917	0.922
17.6	1.209	1.217	90	1.069	1.056
20.1	1.250	1.257	Standard deviation = 0.005		
25.1	1.332	1.338			
30.2	1.420	1.422			
40.2	1.590	1.591			
49.9	1.754	1.760			
60.0	1.949	1.940			
72.1	2.174	2.163			
Standard devtation = 0.007					

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Comprison of the experimental and calculated values (Table 2) shows that the standard deviations are quite low and individual deviations do not exceed two per cent. for both the liquids except for the single temperature of 45°, which is very near the freezing point of Chlorobenzene and where the deviation is expected to be large. In the case of Aniline, calculations could not be carried out near the freezing point since the negative value of constant c_2 makes the variable z turn negative near the freezing point. This, however, does not detract from the validity of eq. (1) over the rest of the region.

Thus it is found that the proposed eq. gives a good agreement between the experimental and calculated values of fluidity over comparatively wide temperature range, which extends below the transition temperature of $T/T_c \leqslant 0.46$. However very near the freezing points of the liquids, the equation does not give acceptable results, which is only to be expected.

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Solute-Solvent Interactions in Solutions of Some Ammonium Salts in Aqueous Dioxane

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Solute-solvent interactions are reported in the concentration range from the conductance studies of N_4HCl, NH_4Br and NH_4NO_3 in 10, 20 and 30 weight per cent. of Dioxane-water mixtures at 25°, 30°, 35° and 40°. Experimental data were analysed for limiting equivalent conductance, Λ_0, on the basis of Owen's method. An attempt is made to discuss the results in terms of solute-solvent interaction from the temperature-coefficient of the Walden product, $\Lambda_0\eta_0$ of the electrolyte solutions. Further, $\Lambda_0\eta_0$ is also found to exhibit a linear relationship with the dielectric constant, D. of the dioxane-water mixtures.

FREQUENT use of non-aqueous solvents as media for organic and inorganic reactions has led to increasing interest in the transport properties of electrolytes in solution. Electrolyte behaviour in solutions is revealed by conductance and viscosity investigations which elucidate directly from experimental measurements the nature of ion-ion and ion-solvent interactions. Recently, there have been a number of studies on conductance of electrolytes in many non-aqueous solvents like DMSO[1,2], Sulfolane[3], Acetonitrile[4], Acetone[5], Methylethylketone[6], tetramethylurea[7], aliphatic alcohols[8] and Ethyleneglycol[9], etc. Conductance measurements in binary mixed solvents have also been widely used for the investigations of solute-solvent interactions in electrolyte solutions. Fuoss *et al.* have extensively studied the conductance behaviour of tetraalkylammonium salts in various binary mixed solvents, namely, MeOH-benzene[10], MeOH-methylethylketone[11], MeOH-CCl_4[12], EtOH-CCl_4[13] and dioxane-water[14,15] mixtures. Conductance of some alkali halides in dioxane-water have also been reported recently by Fuoss *et al.*[16].

The present study has been carried out with a view to: (i) report the limiting equivalent conductivities of some ammonium salts in dioxane-water mixtures and to (ii) study the temperature coefficient of the Walden product, $\Lambda_0\eta_0$ and (iii) its variation with the dielectric constant of the dioxane-water mixtures.

Experimental

Electrolytes *viz.*, NH_4Cl, NH_4Br and NH_4NO_3, in the present study, were of Analar grade and were used as such without further purification.

Dioxane (G. R.) was purified by refluxing over sodium for 6 hours followed by distillation. The specific conductance for the purified dioxane was found to be negligible. Water of specific conductance 1.3×10^{-6} ohm^{-1} cm^{-1} was used for making, by weight, the aqueous mixtures of dioxane.

All solutions were made by weight and conversion of the molality to molarity was done by using the usual relationship[17].

Conductance measurements were carried out at 25°, 30°, 35° and 40°, in the manner similar so that reported in our earlier publications.[18-20]

Results and Discussion

The derived parameters, limiting equivalent conductances, Λ_0 and the Walden products, $\Lambda_0\eta_0$ for the electrolytes in dioxane-water mixtures of different compositions, and at different temperatures, are summarized in Table 1.

TABLE—1 VALUES OF Λ_0 AND $\Lambda_0\eta_0$ FOR NH_4Cl, NH_4Br AND NH_4NO_3 IN DIOXANE-WATER MIXTURES AT VARIOUS TEMPERATURES

Weight per cent., Dioxane	Electrolyte	Temperature (°C)	Λ_0 ($S.cm^2.mol^{-1}$)	$\Lambda_0\eta_0$ ($S.mol.^{-1}N.S.10^{-4}$)
10	NH_4Cl	25	99.50	1.238
		30	141.50	1.255
		35	156.70	1.273
		40	180.50	1.291
20	NH_4Cl	40	147.49	1.385
30	NH_4Cl	40	128.50	1.445
10	NH_4Br	25	114.05	1.420
		30	151.07	1.340
		35	156.52	1.271
		40	167.50	1.190
20	NH_4Br	40	151.00	1.420
30	NH_4Br	40	140.50	1.580
10	NH_4NO_3	25	115.50	1.438
		30	165.16	1.465
		35	176.50	1.492
		40	208.67	1.520
20	NH_4NO_3	40	173.10	1.625
30	NH_4NO_3	40	169.50	1.794

Λ_0 values for the electrolytes in dioxane-water mixtures were estimated from a method proposed by Owen[21]. This is based on the conductance equation :

$$\Lambda = \Lambda_0 - SC^{\frac{1}{2}} + Ac\log c + Bc \quad \ldots \quad (1)$$

Where Λ is the observed equivalent conductance at the concentration C, S refers to the limiting Onsager slope, A and B are the constants.

For extrapolation purposes, equation (1) is written as :

$$\frac{\Lambda + SC^{\frac{1}{2}} - \Lambda_0}{C} = A \log c + B \quad \ldots \quad (2)$$

so that when the left-hand side is plotted against log c, a straight line will result if the correct value of Λ_0 has been chosen. This choice is made by trial and error. The values of Λ_0 for the electrolytes in aqueous mixtures of dioxane, which gave the best straight lines according to relation (2), were therefore estimated and these have been recorded in the Table I.

Viscosities of the aqueous mixtures of dioxane, η_0 for the evaluation of Walden products, $\Lambda_0\eta_0$ are summarized in Table 2.

TABLE—2 VISCOSITIES OF DIOXANE-WATER MIXTURES

Weight Per cent., Dioxane	Temperature (°C)	Viscosity $10^4.\eta_0(N.S.m^{-2})$
10	25	12.45
	30	8.87
	35	8.12
	40	7.15
20	40	9.39
30	40	11.25

Variations or Walden product with Temperature :

Experimental data for the temperature variation of the Walden product of electrolytes in aqueous

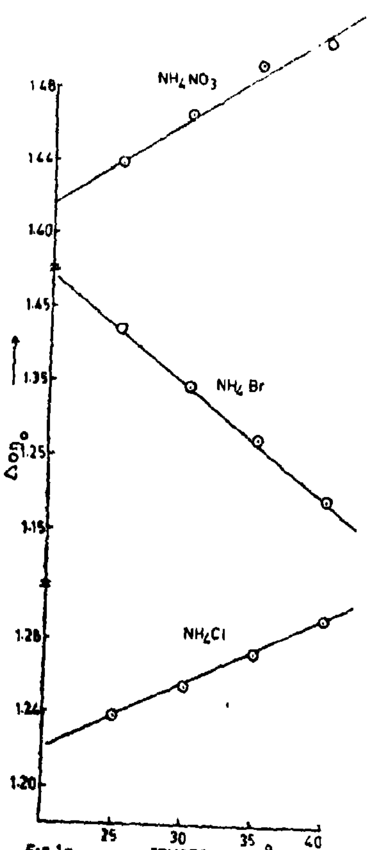


Fig. 1a DEPENDENCE OF $\Lambda_0\eta_0$ ON t

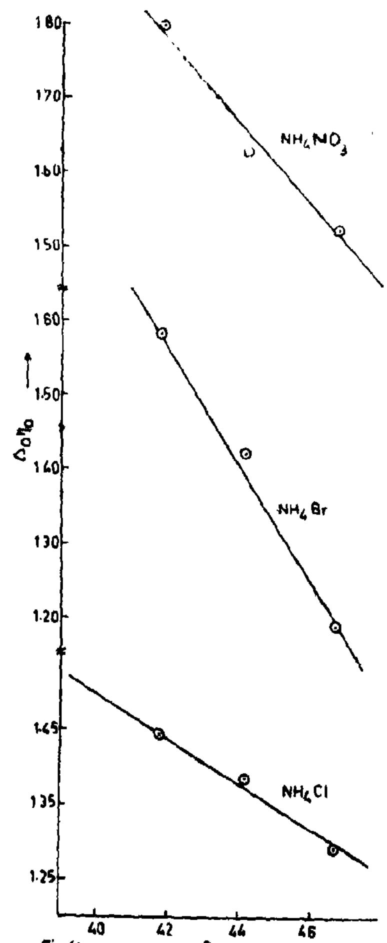


Fig. 1b DEPENDENCE OF WALDEN PRODUCT ON D

solutions and in organic solvents are scanty. Only a few studies on the variation of Walden product with temperature in aqueous solutions and in organic solvents[20,23], have recently, been reported in the literature.

Structural effects on the conductance of ions in aqueous solutions are derived by a comparison of their Walden products in aqueous and non-aqueous solutions and at different temperatures and pressure[24-26]. Thus in the case of large Walden products, their negative temperature coefficients[27], have been attributed to decrease in the structure of the solvent, which can be attributed to the structure-breaking characteristic of the electrolyte in the solvent, whereas positive temperature coefficient have been attributed to the increase in the structure of the solvent which in turn refers to the structure-making characteristic of the electrolyte.

$\Lambda_0\eta_0$ versus t(°C) plots for NH_4Cl, NH_4Br and NH_4NO_3 in aqueous dioxane (10%. by weight) are found to be linear as shown in Figure 1(a).

Positive temperature coefficients of the Walden products for NH_4Cl and NH_4NO_3 in 10% dioxane-water mixture shown in Figure 1(a), can, therefore, be attributed to the structure-making characteristic of these electrolytes in this mixture. Further, structure-making has also been attributed to positive solvation[28], whereas the structure-breaking has been attributed to the negative solvation of the electrolytes in the solvent. Greater positive slope of the $\Lambda_0\eta_0$ vs. t(°C) plot for NH_4NO_3 than NH_4Cl in 10% dioxane-water mixture suggests that NH_4NO_3 acts as a better structure promotor than NH_4Cl in this mixture or in other words, positive solvation is greater in NH_4NO_3 solutions of 10% dioxane-water than NH_4Cl solutions in the same solvent mixture. The greater structure-making in case of NH_4NO_3 than NH_4Cl can be attributed to the fact that NO_3^- ion being smaller in size than the corresponding Cl^- ion (NH_4^+ being common) fits well into the vacant sites[29] of the solvent matrix.

$\Lambda_0\eta_0$ versus t(°C) plots in Figure 1(a) show a negative temperature coefficient in case of NH_4Br solutions in 10% dioxane-water mixture. This suggests that it acts as a structure-breaker in this mixture or in other words, negative solute-solvent interaction is predicted in NH_4Br solutions. This decrease in the structure of the solvent in this case can be attributed to the greater ionic[30] size of Br^- ion than both the Cl^- and NO_3^- ions.

From, Figure 1(b) it is also observed that the plots of Walden product. $\Lambda_0\eta_0$ for NH_4Cl, NH_4Br and NH_4NO_3 solutions in aqueous mixtures of dioxane (10, 20 and 30% by weight at 40°) versus the dielectric constant. D. of these mixtures are linear.

Acknowledgement

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NOTES

Crystal Data on $ZnTaCuO_4$

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A survey of recent literature on the ternary oxides of the chemical formula $XYZO_4$ showed that the compound $ZnTaCuO_4$ has not been synthesized. Earlier we reported[1] the crystal structure of $ZnNbCuO_4$ which is found to have a face-centered orthorhombic structure. The compound reported here may be regarded as a substitution of Ta^{5+} ions for Nb^{5+} ions in $ZnNbCuO_4$, since Nb^{5+} and Ta^{5+} ions have the same oxidation number and comparable ionic radii[3] (Ta^{5+}=0.71 and Nb^{5+}=0.70A).

The compound has been prepared for the first time. It was prepared by intimately mixing together the appropriate oxides[3] of A. R grade in proper molar ratio. The mixture was heated in air at 950° for 70 hours. The X-ray diffraction pattern recorded on a Debye-Scherrer camera (114.6 mm diameter) using filtered copper radiation indicated the presence of a single phase. The three principal diffraction lines as given in ASTM data of the reacting oxides were absent in the pattern. The crystallographic results are given in Table 1. All the observed reflections are indexed on the basis of orthorhombic unit cell having a = 8.58 ± 0.002A, b = 8.86 ± 0.002A and c = 9.54 ± 0.002A. It is evident from the observed reflections that the Bravais lattice is primitive. This clearly shows that the crystal structure of $ZnTaCuO_4$ is different from that of $ZnNbCuO_4$ and hence Ta^{5+} ions do not substitute Nb^{5+} ions in the crystal structure.

TABLE—1

d	2.597	3.12	1.764	4.766
I/I_0	100	70	60	15

Rad : = 1.54 A
Filter Nickel
Dia : 11.46 cm D. S. Camera
Int : Visual

Sys : Orthorhombic SG :—
a_0 8.58 b_0 8 86 c_0 9.54

$ZnTaCuO_4$
Zinc-Tantalum-Copper Oxide.

d in A	I/I_0	h k l	d in A	I/I_0	h k l
4.77	15	0 0 2	1.34	5	2 6 2
4.33	15	2 0 0	1.29	10	6 3 0}
3.90	15	2 0 1			4 4 4}
3.74	20	1 1 2	1.26	20	5 1 5
3.56	10	2 1 1	1.24	5	1 7 1
3.23	10	0 2 2	1.20	5	7 1 1
3.12	70	2 2 0	1.18	10	7 2 0}
2.97	20	0 3 0}			6 2 4}
		1 0 3}	1.16	25	3 7 0
2.68	35	1 3 1	1.14	5	7 2 2
2.60	100	2 2 2	1.12	10	2 4 7
2.50	40	0 3 2	1.09	20	3 7 3
2.38	40	0 0 4	1.06	<5	8 1 1
2.17	45	4 0 0	1.02	<5	2 4 8
2.12	50	3 0 3	1.00	<5	0 8 4
1.97	5	2 4 0	0.996	10	1 6 7
1.94	10	4 2 0	0.951	5	7 2 6
1.76	60	0 2 5	0.928	10	0 6 8
1.73	30	3 3 3	0.906	5	0 8 6
1.67	20	5 1 1	0.877	15	0 9 5
1.65	80	3 4 2	0.861	5	0 6 9
1.61	15	0 4 4	0.846	10	6 4 8
1.55	30	4 4 0	0.829	5	9 5 2
1.48	50	0 6 0	0.819	10	6 3 9
1.43	15	5 0 0	0.807	5	1 8 8
1.41	50	0 6 2	0.788	20	8 2 8
1.37	10	6 0 2	0.782	10	9 0 7
			0.779	10	11 0 0
			0.776	5	6 7 7

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Stability Constants of Some Rare Earth-chelates of 3-(N,2-hydroxy-α-methyl-benzylidene)imino Propionic Acid

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A survey[1-3] of the literature has indicated that no work has been done on La(III), Ce(III), Pr(III), Nd(III), Sm(III) and Gd(III) chelates of 3-(N,2-hydroxy-α-methyl-benzylidene)imino propionic acid ($H_2\beta P$) Schiff base derived from *o*-hydroxy-acetophenone and β-alanine. Hence the work on the potentiometric studies of these chelates was undertaken. The measurements were carried out by the method of Irving and Rossotti[4] at 25°, 30° and 35° in aqueous media (μ=0.1M, 0.05M and 0.01M $NaClO_4$).

For the evaluation of stability constants, the following solutions (total volume 25.0 ml) were titrated against the standard carbonate-free sodium hydroxide (0.1M) and the titration curves had the usual shapes. (1) 5.0 ml. 0.01M $HClO_4$+2.5 ml., 1.0M $NaClO_4$+17.5 ml. water, (2) 5.0 ml., 0.01M $HClO_4$+2.5 ml. 1.0M $NaClO_4$+10.0 ml. 0.01M $H_2\beta P$+7.5 ml. water, and (3) 5.0 ml., 0.01M $HClO_4$+2.5 ml., 1.0M $NaClO_4$+10.0 ml., 0.01M $H_2\beta P$+2.0 ml, 0.01M Metal-ion solution+5.5 ml., water.

The results of the stability constants of the rare earth chelates were obtained at different ionic strengths at 25°, 30° and 35° (Table 1). The formation curves of the metal-chelates suggest the formation of 1 : 2 complexes. The stabilities of the metal-chelates follow the order, La(III)<Ce(III)<Pr(III)<Nd(III)<Sm(III)<Gd(III), which is in accordance with lanthanide contraction.

TABLE—1 DISSOCIATION CONSTANTS OF $H_2\beta P$ AND STABILITY CONSTANTS OF ITS RARE EARTH-CHELATES AT DIFFERENT IONIC STRENGTHS (μ)

Dissociation stability constants	μ at 25°			μ at 30°			μ at 35°		
	0.1 M	0.05 M	0.01 M	0.1 M	0.05 M	0.01 M	0.1 M	0.05 M	0.01 M
					H_2BP				
$\log K_1^H$	10.93	10.94	10.95	10.89	10.90	10.92	10.86	10.88	10.89
$\log K_2^H$	9.92	8.95	8.96	8.85	8.87	8.89	8.79	8.81	8.83
					La(III)				
$\log K_1$	6.97	6.99	7.00	6.95	6.97	6.99	6.94	6.96	6.98
$\log K_2$	5.85	5.87	5.38	5.34	5.36	5.39	5.33	5.35	5.37
					Ce(III)				
$\log K_1$	7.82	7.84	7.85	7.78	7.80	7.82	7.75	7.76	7.79
$\log K_2$	6.25	6.27	6.28	6.24	6.26	6.28	6.23	6.25	6.27
					Pr(III)				
$\log K_1$	8.31	8.33	8.34	8.29	8.31	8.34	8.27	8.29	8.31
$\log K_2$	6.65	6.67	6.68	6.63	6.65	6.67	6.61	6.63	6.65
					Nd(III)				
$\log K_1$	8.67	8.69	8.70	8.66	8.68	8.70	8.65	8.67	8.69
$\log K_2$	6.90	6.92	6.93	6.88	6.90	6.93	6.86	6.88	6.90
					Sm(III)				
$\log K_1$	9.11	9.13	9.14	9.10	9.12	9.13	9.09	9.11	9.13
$\log K_2$	7.13	7.15	7.17	7.11	7.12	7.13	7.09	7.11	7.13
					Gd(III)				
$\log K_1$	9.46	9.48	9.51	9.41	9.43	9.45	9.36	9.38	9.39
$\log K_2$	7.29	7.31	7.34	7.27	7.29	7.31	7.25	7.27	7.31

Precision *p*H-meter type OP : 205 No. 837 with glass-calomel assembly was used. $H_2\beta P$ was synthesised by the general procedure reported earlier[5], m.p. 197°, found C, 63.68 ; H, 6.19 ; N, 6.65 ; calcd. for $C_{11}H_{13}NO_3$. C, 63.76 ; H, 6.28 ; N, 6.76%. All the chemicals used were either BDH or Ridiel reagents. The standard solutions of $H_2\beta P$, metal nitrates and sodium perchlorate were prepared in doubly-distilled water.

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Spectrophotometric Determination of Ti(IV) and V(V) with 5,6, Dibromo, 2,3,4, Trihydroxyacetophenone

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ALTHOUGH a number of reagents have been reported[1-6] in the spectrophotometric analysis of titanium and vanadium there is always a search for new and better reagents. The present paper reports the application of 5,6 dibromo, 2,3,4, trihydroxy-acetophenone (DBTHAP) in the spectrophotometric estimation of V(V) and Ti(IV). The proposed reagent is more sensitive than many others reported in the literature for the same purpose[1-6]. The method also suffers from minimum interference from many cations and anions commonly encountered in the spectrophotometric analysis of vanadium and titanium.

DBTHAP forms an orange yellow complex with Ti(IV) (λ_{max} 390 nm) and a green complex with V(V) (λ_{max} 600 nm) in the *p*H range 3 and 5. The vanadium complex is stable for about half an hour while the titanium complex is stable for more than 12 hours. The spectrophotometric properties of the complexes are given in Table 1. Beers law

TABLE—1

SPECTROPHOTOMETRIC DATA OF Ti(IV) AND V(V) COMPLEXES WITH DBTHAP

Metal	λ_{max} nm	$\epsilon \times 10^3$	Sandells sensitivity $\mu g/cm^2$
Ti(IV)	390	17.5	0.0027
V(V)	590	3.5	0.0145

was studied and found to be obeyed between 0.15 and 2 ppm of titanium and 0.5 and 8 ppm of vanadium. The optimum concentration range for the effective determination as evaluated by Ringboms method was found to be 0.5 to 1.5 ppm of Ti(IV) and 3 to 6 ppm of V(V). The molar composition of the complexes determined by the Jobs method was found to be 1 : 1 in both the cases.

The effect of diverse ions was studied by adding to V(V) or Ti(IV) solutions, various cations and anions 10 times in excess. The limit of tolerance was set to $\pm$ 0.5% deviation in the absorbance reading. It was found that ions like Cu^{2+}, Ni^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Mn^{2+}, Cl^-, Br^-, I^-, CH_3COO^-, ClO_4^- do not interfere, however, cations like UO_2^{2+}, Th^{4+}, Zr^{4+} and Fe^{3+} interfere seriously and should be absent.

Experimental

All chemicals used were of A.R. grade. Spectrophotometric studies were carried out on Beckman DU-2, UV-visible spectrophotometer.

Preparation of the Reagent :

The preparation of 2,3,4-trihydroxyacetophenone (THAP) was carried out by the procedure given in the literature[7]. The bromination of THAP was carried out as follows :

A cold (~10°) solution of bromine (1 g) in chloroform (20 ml) was added to a cold suspension of THAP (1.68 g) in chloroform (20 ml) and the resulting mixture was stirred for 12 hours at temperature below 10°. Pale yellow crystals were separated after the addition of petroleum ether (40-60°). The product was purified by column-chromatography on silicagel using chloroform as eluent to give 5.6 dibromo, 2,3,4, trihydroxyacetophenone (DBTHAP) as pale yellow crystals. The composition of DBTHAP was verified by I. R. and elemental analysis.

Procedure :

To an aliquot containing up to 1.5 ppm of Ti(IV) or 6 ppm of V(V) was added 4 ml of $1 \times 10^{-3} M$ in case of titanium and 4 ml of $8 \times 10^{-3} M$ alcoholic solution of the reagent in case of vanadium. The *p*H of the mixture was adjusted to 4.5, with acetate buffer and the solution diluted to 25 ml. The absorbance readings were taken at the λ_{max} of the complexes against the corresponding reagent blank. The amounts of the metals were calculated from the calibration curves drawn under identical conditions.

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Potentiometric Study of the Complexes of Indium(III) with Some Azo Dyes

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SPECTROPHOTOMETRIC study of indium(III) complexes with 3-hydroxy-4-[(6-hydroxy-*m*-tolyl) azo]-1-naphthalene sulfonic acid (trivial name: Calmagite) (CLM), 3-hydroxy-4-[(2-hydroxy-naphthyl)azo]-1-naphthalene. Sulfonic acid(trivial name: Solochrome Dark Blue) (SDB), 4-(2-pyridylazo)-resorcinol (PAR) and 1-(2'-pyriydlazo)-2-naphthol (PAN) has been reported by different workers[1-8]. However, the potentiometric study involving the stepwise formation of these complexes, has been reported for the first time in the present communication. The studies have been carried out with SDB and CLM in aqueous media. However, due to the low solubility of PAR and PAN in aqueous media the studies with these ligands have been made in 50% dioxan-water media. The "Practical" proton-ligand stability constants of the ligands and the metal-ligand stability constants (stepwise) have been obtained by Bjerrum-Calvin titration technique[9,10] as used by Irving and Rossotti[11].

Experimental

Reagents: A stock solution (0.02 *M*) of $In(NO_3)_3.5H_2O$ (Schuchardt, Munchen) was prepared in calculated quantity of perchloric acid and the metal content was estimated as 8-hydroxy quinolinate[12]. The stock solutions (0.001*M*) of CLM (B.D.H.) and SDB (B.D.H.) were prepared in double distilled water. The stock solutions (0.005*M*) of PAR (B.D.H.) and PAN (E.Merck) were prepared in purified dioxan[13]. All these ligand solutions were standardised potentiometrically.

Solutions of carbon dioxide free 0.5*M* sodium hydroxide (E. Merck) and 0.5*M* perchloric acid (E. Merck) were prepared and were standardised potentiometrically. The stock solution (1.0*M*) of sodium perchlorate was prepared by dissolving AnalaR (Riedel) $NaClO_4.H_2O$ in double distilled water.

A *p*H-meter (Beckman model H-2) with a glass-calomel electrode assembly was used to determine the change in hydrogen ion concentration of the solutions, using a KNO_3 salt bridge. A thermostat with resulting accuracy of ± 0.2° was used.

Titration Procedure: Three mixtures were prepared containing acid, acid+ligand and acid+ligand+metal ion, such that the concentrations of common ingredients were indentical in different cases. The ionic strength ($\mu = 0.2M$) was maintained by adding neutral sodium perchlorate. The ratio between the metal content and the ligand was kept at 1 : 5. The difference in the amount of sodium hydroxide utilised for the last two titrations was taken as a measure of the extent of complexation.

Results and Discussion

Stoichiometry:

For In(III)-SDB system it was observed that in the metal titration curve, four extra moles of NaOH were required in comparison to ligand titration curve before a steep rise was observed. This indicates that 1 : 2 complex formation takes place and there is liberation of protons during chelation, from the two hydroxy groups present at ortho position to azo group. Similar results have been observed for In(III)-CLM system, which is expected also because SDB differs from CLM only in the hydrocarbon residue.

For In(III)-PAR and In(III)-PAN systems it was observed that in comparison to ligand titration curve approximately 2 extra moles of NaOH were required before finally an inflection was observed in the metal titration curve indicating that 1 : 2 complex formation takes place and that there is liberation of protons during chelation from the hydroxy group present at the ortho position to azo group.

Proton-ligand stability constants:

The formation curves for the proton-ligand systems of CLM and SDB drawn between $\bar{n}_A$ and *p*H were found to be extended between 0 and 2 in the $\bar{n}_A$ scale, thus showing complete dissociation of $—SO_3H$ group.

The formation curves for the proton-ligand systems of PAR and PAN drawn between $\bar{n}_A$ and "*p*H-meter reading" were found to be extended between 0 and 3 for PAR and between 0 and 2 for PAN in the $\bar{n}_A$ scale.

The values of log K_1 and log K_2 for CLM, SDB, PAR and PAN and log K_3 for PAR obtained by the method of interpolation at various $\bar{n}_A$ values having error limits ± 0.05 are summarised in Table 1.

TABLE—1

PROTON-LIGAND STABILITY CONSTANTS AT 25° AND μ=0.2

Ligand	log K_1	log K_2	log K_3
SDB	12.87	7.01	–
CLM	12.15	8.23	–
PAR*	12.36	6.54	2.49
PAN*	12.17	1.96	–

* Experiments in 50% dioxan

Metal-ligand stability constants:

In case of SDB, CLM and PAR systems the reactants had intense colour at *p*H≃7.0, rather the solution showed opalescence and in case of In(III)-

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PAN systems precipitation of the complex was observed at $pH \approx 5.0$. Hence, the portion of the titration curves above these pH values could not be used for obtaining the formation function $\bar{n}$. In order to obtain stability constants the formation curves were drawn between $\bar{n}$ and pL. The approximate values of log K_1 and log K_2 were obtained from the formation curves by reading them at $\bar{n}=0.5$ and 1.5 respectively. The values were not considered to be reliable because log $K_1/K_2<3.0$. Therefore, the values obtained have been further refined by least squares method. The values of stability constants are summarised in Table-2.

TABLE—2

METAL-LIGAND STABILITY CONSTANTS AT 25° AND μ=0.2

System	log K_1	log K_2
In(III)-SDB	16.48	14.66
In(III)-CLM	17.09	14.87
In(III)-PAR*	12.54	11.46
In(III)-PAN*	12.19	10.57

*Experiments in 50% dioxan

Among the azo dyes the order in the stability constant values was found to be CLM>SDB>PAR >PAN. But the values of log K_1/β^H showed that the complexing tendency of PAR and PAN for In(III) was more than that of CLM and SDB. This may be due to the presence of stronger complexing group for In (III), like pyridyl nitrogen in the former ligands.

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Some Anionic Mixed-Ligand Complexes of Cobalt(II)

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THOUGH anionic complexes of cobalt(II) of the type $[CoX_4]^{-2}$, where X is halogen or pseudohalogen have long been studied[1-5] in detail as typical tetrahedral compounds, little has been done to change the stereochemistry of these complexes by reacting with other nitrogen, oxygen or sulphur ligands. To increase the coordination number, particularly to synthesise compounds of coordination number five, we have been trying to synthesise anionic mixed-ligand complexes starting from these type of tetrahedral compounds. In this communication, we report a number of tetra-, penta- and hexacoordinated mixed-ligand (thiocyanate) complexes, using different ligand donor atoms.

Experimental

All the chemicals used were of AnalaR grade. An ethanolic solution of cobalt thiocyanate was treated with an ethanolic solution of tetramethylammonium thiocyanate in 1 : 2 proportion when blue crystalline compound of ditetramethylammonium tetrathiocyanato cobalt(II) was separated out. This was then filtered, washed with ethanol and dried *in vacuo*.

The mixed-ligand complexes were prepared, by adding requisite amount (1 : 2 ratio) of ligands separately to ethanolic suspension of ditetramethylammonium tetrathiocyanato cobalt(II) and refluxing for about 30 minutes. On cooling crystalline compounds were separated out which were then filtered, washed with ethanol followed by ether and dried in vacuo.

Metal and thiocyanate in the complexes were determined by complexometric E.D.T.A. method and nitrogen by micro analysis. Conductance was measured in M/1000 acetone medium using Toshniwal conductivity bridge. Magnetic susceptibility measurement were made over solid specimens by Gouy method. IR spectra were recorded on KBr phase using Perkin-Elmer-221 spectrophotometer. Electronic spectra were recorded using M/100 (chloroform base) solution by Hilger-Watt U. V. Speck spectrophotometer. Relevant analytical, conductance and magnetic susceptibility and spectral data are given in Table 1.

TABLE—1 ANALYSIS, CONDUCTANCE, MAGNETIC SUSCEPTIBILITY AND ELECTRONIC SPECTRAL DATA

Compounds	Colour and form	%cobalt Found	%cobalt Reqd	%N Found	%N Reqd	%thiocyanate Found	%thiocyanate Reqd.	Λ mhos cm²	μ_{eff} (b.m)	max (ϵ) k.k.
$[Me_4N][Co(SCN)_3DEA)]$	Deep blue crystalline	14.94	15.35	17.95	18.23	45.98	45.31	150	4.4	16.1 (1570) 8.0 (220)
$[Me_4N][Co(SCN)_3(Quin)]$	—do—	9.64	9.87	11.52	11.76	38.13	38.48	145	4.5	16.5 (1580) 8.1 (210)
$[Me_4N]_2[Co(SCN)_4$o-ph.D.A.]	Black crystalline	10.38	10.77	20.17	20.47	40.23	40.58	238	4.9	18.8 (40) 8.5 (20)
$[Me_4N]_2[Co(SCN)_3Pdtc]$	Green crystalline	10.45	10.89	15.28	15.53	31.87	32.16	280	4.7	19.1 (61)
$[Me_4N]_2[Co(SCN)_3Oxin]$	—do—	10.83	11.20	15.72	15.99	32.95	33.29	245	4.7	19.0 (68)

DEA = Diethylamine, Quin = Quinaldine, o-ph.D.A. = o-phenylenediamine. Pdtc. = Piperidyldithiocarbamate.

Results and Discussion

On the basis of analysis and conductance data, the complexes have the composition [L] $[Co(NCS)_3B]$ where B is diethylamine and quinaldine; $[L]_2$ $[Co(NCS)_3B]$ where B is piperidyldithiocarbamate and oxin and $[L]_2[Co(NCS)_4B]$ where B is *o*-phenylenediamine, and L is tetramethylammonium cation. The first catagory of complexes are deep blue in colour, have magnetic moments characteristic of typical tetrahedral cobalt(II) compounds and are 1 : 1 electrolytes as indicated by their conductance values (Table 1) in acetone medium. *o*-Phenylenediamine complex is a 2 : 1 electrolyte, is black in colour and has magnetic moment characteristic of an octahedral cobalt(II) species. The second type of complexes are green crystalline solids, 2 : 1 electrolytes and have magnetic moment values in between tetrahedral and octahedral cobalt(II) complexes.

In the infrared spectra absorption bands are noticed at 760(s), 955(vs), and 1490(vs) cm^{-1} characteristic of the bands due to tetramethylammonium ion, modified due to complexation. Very sharp absorption bands are observed $\sim 2050\ cm^{-1}$ attributable to $\nu(C=N)$ of thiocyanate. In addition $\nu(C=S)$ and $\nu(C-O)$ bands have been observed at 1235 and 1200 cm^{-1} for the thiocarbamate and oxin complexes. In case of the oxin complex $\nu(O-H)$ has disappeared indicating coordination of the oxin molecule through the hydroxyl oxygen. Evidence for the coordination of the bases have been further substantiated by appearance of bands $\sim$360-370 cm and $\sim 450\ cm^{-1}$ in the low frequency region assignable to $\nu(M-N)$ and $\nu(M-O)$ (in case of oxin) respectively and $\nu(M-S)$ at 260 cm^{-1} for the dithiocarbamate.

In the electronic spectra of complexes with quinaldine and diethylamine two absorption bands are noticed ~ 16.0 and ~ 8.0 *k.k.* region attributable to ${}^4A_2 \rightarrow {}^4T_1(P)$ and ${}^4A_2 \rightarrow {}^4T_1(F)$ transition respectively, the other transition is not observed probably because of its very weak intensity due to orbital selection rule. The high value of the ${}^4A_2 \rightarrow {}^4T_1(P)$ transition and magnetic moment values support a tetrahedral configuration for these two complexes. Two absorption bands are also observed for the *o*-phenylenediamine complex at 18.8(40) and 8.5(20) *k.k.* region attributable to ${}^4T_1(F) \rightarrow {}^4T_1(P)$ and ${}^4T_1(F) \rightarrow {}^4T_2$ transition. The intensity of the ${}^4T_1(P)$ band and magnetic moment of the complex suggests a spin free octahedral configuration. Only one absorption band was noticed in ~ 19.1 *k.k.* region for complexes with dithiocarbamate and oxin, the other band probably being outside the range of spectrophotometer used. Intensity of this band is nearer to that of an octahedral complex, but from analysis, conductance and the comparative low magnetic moment value suggest these two complexes to be presumably penta-coordinated. This has been supported by an earlier report by Zinde *et al*[6].

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Mixed-ligand complexes of Cobalt(III) containing Trimethylenediamine and Some Bidentate Ligands

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THERE has been considerable interest on the syntheses and optical properties of mixed-ligand heterochelate complexes of cobalt(III) containing ethylenediamine and bidentate ligands[1]. Very little has appeared on similar heterochelate complexes containing trimethylenediamine[2-8]. In this preliminary communication we report the syntheses of some new cobalt(III) heterochelates, the ligands used being trimethylenediamine, biguanide, picolinic acid, acetylacetone, acetoacetanilide, benzoylacetanilide and malonic acid.

Preparation of the complexes

A. For complexes with the ligands biguanide, picolinic acid, acetylacetone, acetoacetanilide and benzoylacetanilide – To an aqueous solution of *trans*-$[CoCl_2(tn)_2]Cl$ (3.1 g, 0.01 mole in 20 ml) an aqueous or ethanolic solution of the appropriate ligand (0.01 mole) was added and the *p*H of the solution was adjusted to 7. In case of biguanide an aqueous neutralised solution of biguanide hydrochloride (2.3 g, 0.01 mole) was added to the *trans*-$[CoCl_2(tn)_2]Cl$ solution (3.1 g, in 20 ml) which was previously neutralised to *p*H 7 with 2N NaOH. The mixture was heated on a steam bath for 2-3 hrs. The *p*H of the solution was finally adjusted to 6.5 with 2N HCl. This was cooled in ice for 1 hr. and the separated red precipitates were filtered, washed with ice-cold water followed by 95% ethanol. Water followed by acetone was used for washing in case of acetoacetanilide and benzoylacetanilide complexes. The complexes were recrystallised from minimum amount of water and finally dried *in vacuo*. Yield = 30-50%.

B. $[Co(mal)(tn)_2]Cl.3H_2O$ – To an aqueous solution of $[Co(CO_3)(tn)_2]Cl.H_2O$ (3.2 g, 0.01 mole in 20 ml) an aqueous solution of malonic acid (1 g, 0.01 mole in 10 ml) was added. The mixtnre was heated on a steam bath for 1 hr. and was then concentrated to a small volume, and cooled in ice bath. The separated rose red precipitates were filtered, washed with ice-cold water followed by 95% ethanol, and dried *in vacuo*. Yield = 40%.

The analytical, conductance and electronic spectral data of the complexes are given in Table 1.

The *trans*-dichlorobis(trimethylenediamine) cobalt(III) chloride or carbonatobis(trimethylenediamine) cobalt(III) chloride has been found to react with one molecule of chelating ligand such as biguanide, picolinic acid, acetylacetone, acetoacetanilide, benzoylacetanilide and malonic acid, resulting in the formation of cobalt(III) heterochelate complexes. The conductance measurements in aqueous medium indicate tri-univalent nature of $[Co(bigH)(tn)_2]Cl_3$, bi-univalent nature of $[Co(pic)(tn)_2]Cl_2$, $[Co(acac)(tn)_2]Cl_2$, $[Co(acan)(tn)_2]Cl_2$, $[Co(benzan)(tn)_2]Cl_2$, and uni-univalent nature of $[Co(mal)(tn)_2]Cl$ (ref. 4). The room temperature magnetic susceptibility measurements by the Gouy method indicate that the complexes are diamagnetic. The magnetic data are indicative of octahedral structure of the complexes with d^2sp^3 bonding. The electronic spectra of the complexes exhibit one or two ligand field bands at around 20000 and 28000 cm^{-1} typical of octahedral cobalt(III) complexes[5]. The second band cannot be located in some complexes as it is buried underneath the strong metal ligand charge transfer transitions.

The equivalent weights of the complexes were determined by running the aqueous solutions through H^+ form of a cation exchange resin

TABLE—1. ANALYTICAL, CONDUCTANCE AND ELECTRONIC SPECTRAL DATA OF COBALT(III) HETEROCHELATES[a]

Complex		%Co	%N	%Cl	Λ_M $ohm^{-1}cm^2mole^{-1}$	ν_{max} (ϵ) cm^{-1}
$[Co(bigH)(tn)_2]Cl_3.H_2O$	Found :	13.8	29.0	23.9		20530 (140)
	Reqd :	13.64	29.14	24.62	428	
$[Co(pic)(tn)_2]Cl_2$	Found :	14.5	17.5	17.5		20530 (100)
	Reqd :	14.75	17.50	17.75	228	
$[Co(acac)(tn)_2]Cl_2.H_2O$	Found :	14.5	14.8	17.8		20000 (115)
	Reqd :	14.94	14.18	17.98	268	
$[Co(acan)(tn)_2]Cl_2.H_2O$	Found :	12.3	14.3	14.8		20000 (110)
	Reqd :	12.50	14.84	15.04	230	
$[Co(benzan)(tn)_2]Cl_2$	Found :	11.0	13.9	13.7		20000 (115)
	Reqd :	11.44	13.57	13.76	225	
$[Co(mal)(tn)_2]Cl.3H_2O$	Found :	14.5	13.5	9.0		20000 (70)
	Reqd :	14 81	14.06	8.91	96	28570 (95)

[a]Abbreviations : tn = trimethylenediamine, bigH = biguanide, pic = deprotonated anion of picolinic acid, acac = deprotonated anion of acetylacetone, acan = deprotonated anion of acetoacetanilide, benzan = deprotonated anion of benzoylacetanilide, mal = deprotonated anion of malonic acid.

(*Amberlite IR 120*) column and then titrating the eluate with 0.05N NaOH. The measured values agree well with the theoretical values.

The isolation and characterisation of other salts of the complex cations, optical resolution and chromatographic studies on the complexes are in progress. The syntheses of mixed-ligand complexes using other OO, ON and NN donor ligands are progressing and details will be reported in due course.

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Complexes of Chromyl Chloride

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CHROMYL chloride is reported to form complexes with phosphorous halides[1], amides[2] and titanium tetrachloride[3]. However, its complexes with nitrogen bases (except with pyridine[4]) have not been studied so far. The pyridine complex has also not been studied in details except the elemental analysis. The formation of complexes of chromyl chloride with nitrogen bases and some oxy-donors is being reported here.

Experimental

Chromyl chloride was prepared by the method reported by Hein and Herzog[5]. It was then repeatedly distilled and the fraction distilling at 117°/740 mm was collected.

The nitrogen bases were purified by refluxing over potassium hydroxide and were fractionally distilled. Acetylacetone and acetoacetic acid were purified by fractional distillation.

Complex Formation : Ice-cold solution of chromyl chloride in carbon tetrachloride was added dropwise to excess of ice-cold solution of the base in carbon tetrachloride. Solid product so obtained was filtered, repeatedly washed with carbon tetrachloride and dried in vacuum.

Chromium in the complexes was estimated by heating the complex to 1000-1200° and weighing the residue as Cr_2O_3. Chloride was estimated by Volhard's method.

Conductances of the complexes in N, N-dimethyl formamide were measured in a dip type cell using Toshniwal CLO1/O1 conductometer.

Infrared spectra of chromyl chloride and its complexes (as nujol mulls) were scanned on Perkin Elmer 621, double beam grating spectrophotometer using polythene plates. The mulls were prepared in a dry box.

Results and Discussion

Elemental analysis (Table 1) of the complexes reveals that all the adducts of nitrogen bases with chromyl chloride bear 2 : 1 stoichiometry whereas those of oxydonors (acetylacetone and acetoacetic acid bear 1 : 1 stoichiometry to chromyl chloride. All the complexes are solids at room temperature, sensitive to traces of moisture and stable only in dry atmosphere. The complexes are insoluble in most of the common organic solvents except in N,N-dimethyl formamide in which they exhibit low solubility. The molecular weights of the complexes could not be determined due to their insolubility in the solvents having convenient freezing points.

Molar conductance data of the complexes in N,N-dimethyl formamide (Table 1) reveal that all the complexes are non-ionic in nature.

TABLE—1

PHYSICAL PROPERTIES AND ANALYTICAL DATA OF COMPLEXES OF CHROMYL CHLORIDE

Complex	Colour	m.p(°C)	Molar conductance ($Ohm^{-1}cm^2mole^{-1}$)	%of Cr		%of Cl	
				Found	Calculated	Found	Calculated
$CrO_2Cl_2.2C_5H_5N$	Dark brown	159	8	16.2	16.6	22.5	22.7
$CrO_2Cl_2.2C_5H_{11}N$	Light brown	Decomposes	6	15.8	16.0	22.2	21.9
$CrO_2Cl_2.2C_6H_7N$	Reddish brown	165	9	12.7	12.6	17.0	17.2
$CrO_2Cl_2.2C_6H_{11}N$	Brown	Above 350	5	12.8	13.1	17.7	17.9
$CrO_2Cl_2.C_5H_8O_2$	Greenish brown	—do—	4	19.9	20.4	27.9	27.8
$CrO_2Cl_2.C_4H_6O_3$	Light brown	—do—	5	20.8	20.2	27.8	27.6

The IR spectral data (Table 2) reveal that various bands assigned to the donor molecules have shifted either to the lower or higher region in the spectra of the complexes. The shift of these bands shows the coordination of these molecules.[6-10]

TABLE—2

IR SPECTRAL DATA OF COMPLEXES OF CHROMYL CHLORIDE

Complex	Assignment	Bands (cm^{-1})
$CrO_2Cl_2.2C_5H_5N$	C=C	1630 s
		1605 s
	C=N	1532 m
	Cr=O	950 s
	Cr—Cl	455 s
$CrO_2Cl_2.2C_6H_7N$	C=C	1630 m
		1590 s
	C=N	1550 m
	Cr=O	945 s
	Cr—Cl	445 s
$CrO_2Cl_2.2C_5H_{11}N$	N—H	2725 s
		2520 s
	C—H	2620 w
	H—C—H	1445 s
	Cr=O	940 s
	Cr—Cl	435 s
$CrO_2Cl_2.2C_6H_{11}N$	N—CH_3	1350 m
	Cr=O	950 s
	Cr—Cl	470 m
$CrO_2Cl_2.C_5H_8O_2$	C=O	1560 w
		1510 m
	Cr=O	930 s
	Cr—Cl	435 s
$CrO_2Cl_2.C_4H_6O_2$	C=O	1575 s
		1520 m
	Cr=O	915 s
	Cr—Cl	460 m

Chromium-oxygen band in pure chromyl chloride occurs[11-12] at 984 cm^{-1}, whereas in various complexes the corresponding band appears in the region of 920 cm^{-1}-950 cm^{-1}. Chromium-chlorine band appears at 465 cm^{-1} in chromyl chloride. This band has shifted to the region of 435 cm^{-1}-455 cm^{-1} in the spectra of the complexes. These shifts in the characteristic bands of chromyl chloride reveal the formation of a bond between ligand molecules and chromium of chromyl chloride.

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Synthesis of Few Linear Organopolysilanes

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ALTHOUGH the chemistry of organosilicon compounds has been the subject of considerable study, comparatively little is known about the linear long chain organopolysilanes[1]. The polysilanes appear to be less stable than their carbon counterpart[2] but they are certainly sufficiently stable to make their isolation and characterisation possible. Few methyl or phenyl or both substituted linear polysilanes with various chain lengths were reported in the literature[3]. In connection with the synthesis of polymeric organosilicon compounds having special thermal characteristics, the present communication reports the synthesis of three new linear methyl, phenyl-substituted organopolysilanes (I-III) containing 6, 8 and 10 silicon atoms.

$Ph_3Si-(SiMe_2)_4-SiPh_3$ (I) $\quad$ $Ph_3Si-(SiMe_2)_6-SiPh_3$ (II)

$Ph_3Si-SiPh_2-(SiMe_2)_6-SiPh_2\ SiPh_3$ (III)

The success in the synthesis of the above three polysilanes was due primarily to the ready availability to different α, ω-dihalopolysilanes obtained by the cleavage of dodecamethylcyclohexasilane[4] with phosphorous pentachloride[5d] in sym-tetrachloroethane or with chlorine[5e] in carbon tetrachloride 1, 1, 1, 6, 6, 6-hexaphenyl-2, 2, 3, 3, 4, 4, 5, 5-octamethylhexasilane[5](I) and the polysilane(II) were prepared by the reaction of triphenylsilyllithium[6] in tetrahydrofuran(THF), obtained by the lithium cleavage of hexaphenyldisilane, with 1, 4-dichloro-octamethyltetrasilane[5e] and 1, 6-dichlorododecamethylhexasilane[5e] respectively.

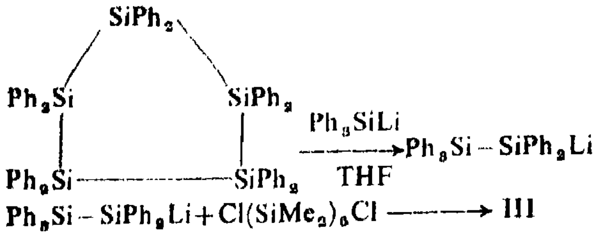
$$Ph_3Si-SiPh_3 \xrightarrow[THF]{Li} 2Ph_3SiLi$$

$$2Ph_3SiLi+Cl(SiMe_2)_4Cl \longrightarrow I$$

$$2Ph_3SiLi+Cl(SiMe_2)_6Cl \longrightarrow II$$

The linear decasilane(III) was prepared by the reaction of pentaphenyldisilyllithium[7] (obtained

from triphenylsilyllithium and decaphenylcyclopentasilane) with 1, 6-dichlorododecamethylhexasilane in THF.



The structures of the above three linear polysilanes were assigned by analytical and spectral evidences. Little quantity of hexaphenyldisilane was formed during the preparation of each of the polysilanes(I-III). This is supported by the previous study of halogen-metal interconversion reaction of phenylsilyllithium compounds with mono and polyhaloalkanes[8].

Experimental

The dodecamethylcyclohexasilane was prepared by the interaction of lithium and dichlorodimethylsilane in THF. 1, 4 and 1, 6-dichloropolysilanes were prepared by the chlorine cleavage of dodecamethylcyclohexasilane in carbon tetrachloride. All reactions were carried out with oven dried glassware in an atmosphere of dry oxygen-free nitrogen. Melting points were recorded in Mel-Temp apparatus. (All experimental work done in the Chemical Laboratory. Iowa State University, Ames, Iowa U.S.A.)

General procedure for the preparation of polysilanes(I-III)

To 0.01 mole of ∝, ω-dihalopolysilane in 50 ml of THF, 0.02 mole of silyllithium compound in THF was added dropwise with stirring. The Gilman Colour Test[9] was negative immediately after the addition was complete. The reaction mixture was hydrolysed with water and the aqueous layer was extracted with ether. The combined organic layers were dried with sodium sulphate, concentrated and cooled when hexaphenyldisilane was separated and indentified through mixed melting point with an authentic sample. It was filtered and the filtrate on evaporation left a residue which was chromatographed over alumina. Petrol ether (60-80°) eluted polysilane compound. Analytical sample was prepared by repeated crystallisation from suitable solvent (vide Table 1).

TABLE—1

Polysilanes	Yield %	M.P. °C	Solvent for cryst.	Analysis[a] C	H	Si
	50	182	Petrol ether (60-80°)	70.31 (70.34)	7.24 (7.19)	22.32 (22.45)
	54	156	,,	66.51 (66.45)	7.33 (7.6)	25.71 (25.9)
I	45	222	Cyclohexane	69.97 (70.2)	7.04 (6.9)	22.76 (22.56)

a. Figure in the parenthesis shows the calculated value.

The pattern of the IR. spectra of the polysilanes (I-III) are comparable, showing peaks around 7.8-8.0μ due to Si – Me and 6.9, 8.9 and 13.5-14.4μ due to Si-Ph groups. No bands due to Si – O – Si and Si – OH groups were noted. The PMR analysis of the three polysilanes gave the ratios of aliphatic to aromatic protons in good agreement with the theoretical values.

Acknowledgement

The author thanks to Dr. Henry Gilman, Iowa State University, Ames, Iowa, U.S.A., for providing research facilities and for his keen interest and encouragement during the investigation.

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Studies on Adsorption Indicators*: Mono- and Bis-hydroxyphenyl Phthalides as Adsorption Indicators in Argentometric Titrations of Bromide and Thiocyanate Ions

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PHENOLPHTHALEIN has been highly recommended in literature by Uzumasa[1], Mehrotra[2], and Akiyama and Yabe[3] as an adsorption indicator in slightly alkaline condition for the argentometric titration of iodide, chloride and thiocyanate ions respectively.

In the present communication phenolphthalein (VIII) and 7 new phenol dyes (I-VII) have been studied for their utility as adsorption indicators. The dyes (I-VII) being : 3-(*p*-hydroxyphenyl)phthalide(I), 3,3-bis(*p*-hydroxyphenyl)4, 5, 6, 7-tetrachlorophthalide(II), 3-acetyl-3-(*o*- or *p*-hydroxyxyphenyl)-4,5,6,7-tetrachlorophthalide(III), 3-(*o*-hydrophenyl)-4,5-dimethoxyphthalide(IV), 3-phenyl-3-(*o*- or *p*-hydroxyphenyl) 2, 3-naphthalide (V),β-1-naphthylphenolsuccinein(VI), β-2-naphthyl-phenol-succinein-(VII) and phenolphthalein(VIII).

Experimental

Material : $AgNO_3$, KBr were A.R.(BDH) and KSCN was I.R.(BDH) grade reagents.

Indicator Solutions, Preparation of dyes[4].

Procedure : $AgNO_3$ from the burette is added slowly, shaking the contents of the conical flask all the time. Complete coagulation leaving the clear supernatant liquid occurs exactly at the equivalence point.

Results and Discussion

The dye 3-(*p*-hydroxyphenyl)phthalide(I) is in some respects better than phenolphthalein(VIII) and can be used in neutral as well as in slightly alkaline condition for bromide ions (0.1 – 0.005 N solutions) and thiocyanate ions (0.1-0.01 N solutions). Rest of the dyes (II-VIII) can only be used in slightly alkaline condition. Thus, for bromide ions (VIII) and II can be used for 0.1-0.005 N solutions ; dyes (III-V) for solutions 0.1-0.02 N) and for thiocyanate ions (dye II can be used for solutions 0.1 – 0.005 N ; dyes I, IV and V for solutions 0.1-0.01 N ; III can be used well for 0.1 N solution). Dyes VI and VII are unsuitable.

Detailed studies of I, II, III, IV, V and VIII have been shown in the given Tables.

* Part I & II, *See J. Indian Chem. Soc.* (1976), **53**, 848-951

TABLE—1 DYES I, VIII AND II USED AS ADSORPTION INDICATORS (FOR THE ESTIMATION OF BROMIDE IONS. CONCN. OF $AgNO_3$ USED : SAME AS KBr, VOL. REQD. 10 ml IN EACH CASE. DYE I HAS BEEN USED IN NEUTRAL AS WELL AS IN SLIGHTLY ALKALINE CONDITION ; AND DYES VIII AND II IN SLIGHTLY ALKALINE CONDITION ONLY.

Dye	Concn. of KBr	Drops of indicator	Transition of colour	Remarks
I	0.1 N	6	yellow suspn.→orange-pink ppt.	(a)
I	0.02 N	6	yellowish-white suspn.→orange ppt.	(a)
I	0.01 N	5	orange-yellow turbidity→orange ppt.	(a)
I	0.005 N	4	orange-yellow turbidity→orange ppt.	(a)
VIII	0.1 N	6	pink tinged-white suspn.→pink ppt.	(b)
VIII	0.02 N	6	pink tinged-white suspn.→violet-blue ppt.	(b)
VIII	0.005 N	4	white suspn.→greenish-ash ppt.	(b)
II	0.1 N	6	yellowish-white suspn.→violet-ash ppt.	(b)
II	0.02 N	6	yellowish-white suspn.→violet-ash ppt.	(b)
II	0.01 N	5	white suspn.→bluish-violet-ash ppt.	(b)
II	0.005 N	3	violet shaded turbidity→light green ppt.	(b)

(a) = complete coagulation and clear supernatant liquid at the end point.

(b) = complete coagulation and faint pink supernatant liquid at the end point.

TABLE—2 DYES (I-V) USED AS ADSORPTION INDICATORS FOR THE ESTIMATION OF SCN^-. CONCN. OF $AgNO_3$ USED : SAME AS KSCN, VOL. REQD. 10 ml IN EACH CASE. CONDITIONS OF TITRATIONS SAME AS MENTIONED IN TABLE 1.

Dye	Concn. of KSCN	Drops of indicator	Transition of colour	Remarks
I	0.1 N	8	orange tinged-white suspn.→orange-pink ppt.	(a)
I	0.02 N	5	white suspn.→orange-pink ppt.	(a)
I	0.01 N	5	orange tinged-white suspn.→orange-pink ppt	(b)
II	0.1 N	8	white suspn.→violet ppt.	(a)
II	0.02 N	8	white suspn.→violet ppt.	(a)
II	0.01 N	5	violet tinged-white suspn→violet ppt.	(a)
II	0.005N	4	violet-white turbid soln.→violet ppt.	(b)
III	0.1 N	8	white suspn.→violet ppt.	(a)
IV	0.1 N	8	violet tinged-white suspn.→violet ppt.	(a)
IV	0.02 N	8	violet-white suspn.→violet ppt.	(a)
IV	0.01 N	6	violet shaded suspn.→violet ppt.	(b)
V	0.1 N	10	white suspn.→violet ppt.	(a)
V	0.01 N	6	white suspn.→orange-violet ppt.	(a)

(a) = immediate coagulation ; at the end point a through light colour developes in the solution like that of the ppt. coagulated, and leaves a clear supernatant liquid.

(b) = delayed coagulation ; end point colour change same as mentioned under (a).

The following points emerge on comparing the above dyes (I – V) with Phenolphthalein :

1. That the dye II is far better than phenolphthalein in slightly alkaline condition for (0.1-0.005 N) solutions while phenolphthalein can only be used for 0.1-0.01 N thiocyanate solutions.

2. That the dye I has the adventage of its being used as an indicator in neutral as well as slightly alkaline condition (for Br^-, 0.1-0.005 N ; for SCN^-, 0.1-0.01 N).

3. That the dyes (III-V) can be used for solutions of higher concentrations in slightly alkaline condition ranging in dilution from 0.1-0-01 N.

4. That the dyes VI and VII are unsuitable for the titrations of bromide and thiocyanate ions.

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Chemical Examination of Flowers of *Asparagus gonocladus* Baker

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ASPARAGUS gonocladus, Baker[1] (N.O. Liliaceae) known as Shakakul in Hindi is used in the indigenous system of medicine for various ailments. Previous studies have shown the presence of asparagine[1] in other species.

The fresh flowers were repeatedly extracted in the cold with successive quantities of methanolic hydrochloric acid (1%). The red coloured combined extract so obtained responded to colour tests for the presence of anthocyanins[2]. Paper chromatographic examination revealed the presence of only one anthocyanin which was crystallised from a mixture of acetone and ether as red crystals, $C_{29}H_{35}O_{17}Cl$, m.p. 165°(d), λ_{max}530 nm, ν_{max}^{Nujol} 3380, 1638, 1555, 1498, 1460, 1432, 1346, 1180, 1042, 932, 910, 886, 820,...,etc. cm^{-1}. The compound on hydrolysis with 7 per cent. sulphuric acid yielded Malvidine chloride, $C_{17}H_{15}O_7Cl$, m.p. above 300°, λ_{max}542 nm, ν_{max}^{Nujol} 1640, 1550, 1500, 1464, 1430, 1350, 1170, 1040,..., etc. cm^{-1}, and glucose (identified by co-chromatography with the authentic sample and osazone formation). The quantitative estimation of sugar moiety by colorimetric method[3] showed the presence of glucose and Malvidine chloride in the molar ratio of 2 : 1. The anthocyanin was identified to be Malvin chloride by mixed m.p. with the authentic sample.

The flowers were washed with ethanol and then exhaustively extracted with 80 per cent. ethanol. The ethanolic extract responded to colour test with ninhydrin for the presence of amino acids. Paper chromatographic examination revealed the presence of an amino acid. Its identity was confirmed by co-chromatography with the authentic sample of asparagine.

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Carboxylation of Pyrazolones and Application of the Products

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IN continuation of our reports on heterocyclic fungicides[1-4], in which it has been noted that 2-pyrazolin-5-one derivatives possess significant fungicidal activity against the rice blast fungus Pyricularia Oryzae, we have tried to synthesise some water soluble carboxy derivaties of 2-pyrazolin-5-ones herein, for their application as systemic fungicides. A compound, to behave as a systemic fungicide must have high water solubility in order to be absorbed by the rice plant from the soil. It has been observed that carboxylation of 2-pyrazolin-5-one nucleus renders it more water soluble.

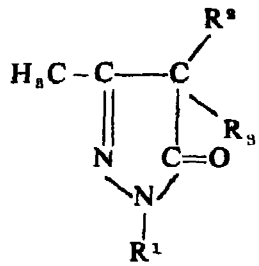
It had been reported[5] that carboxylation of resorcinol can be effected by heating in water with potassium bicarbonate at 100°. As 2-pyrazolin-5-one nucleus has marked similarity with phenolic compounds, the same method is applied here to carboxylate 1-phenyl-3-methyl-2-pyrazolin-5-one and 3-methyl-2-pyrazolin-5-one.

Six carboxy acids were prepared and screened for antifungal activity against the fungus P. Oryzae by the standard method[6]. The details of the observations on these compounds are given in Table 1. It has been observed that all these compounds except compound No. 4, exhibited more fungicidal activity than the corresponding compounds without the carboxy groups. Fungicidal activity of all these later compounds have been reported earlier [1,8].

Amongst these, compounds 2 and 5 are found to be the most effective potential systemic fungicides,

and are now under investigation at C. R. R. I., Cuttack, by pot application.

TABLE—1



Sl. No.	R[1]	R[2]	R[3]	M.P. (°C)	% Yield	Concn. in parts per million	% of inhibition of spore germination
1.	Ph	H	COOH	189	70	1000	95
2.	Ph	NO	COOH	162	95	250	100
3.	Ph	Br	COOH	132	65	1000	80
4.	H	H	COOH	205	70	1000	75
5.	H	NO	COOH	240	90	500	100
6.	H	Br	COOH	196	65	1000	85

Compounds No. 1 and 4 are prepared by the carboxylation method described[6] for resorcinol and also by the method reported elsewhere[7]. The products from both the methods are found to be identical. Compounds No. 2, 5 and 3, 6 are prepared by the methods of nitrosation and bromination respectively as reported earlier[1,8] from this laboratory. The elemental analysis of all the compounds are quite satisfactory.

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Studies on Tripropyltin Dithiocarbamates

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IN continuation to our studies on diorgano dithiocarbamates of organometal moieties, we report the preparation, characterisation, and structure of some new tripropyltin dithiocarbamates of the general formula (Pr_3Sndtc)(where dtc = morpholine-, piperidine-, dibutyl-, N-methylaniline-, diethyl-, N-ethylaniline-dithiocarbamates).

Experimental

Bis(tripropyltin) oxide was obtained from Alfa Inorganics (U.S.A.). Amines and solvents were purified by conventional methods. Physico-chemical measurements were made as reported earlier[1].

A representative method for the preparation of tripropyltin morpholine dithiocarbamate is given below :—

To a mixture of bis(tripropyltin) oxide (10 mmole) and carbon disulphide (10 ml) in chloroform (20 ml), morpholine (20 ml) in the same solvent (10 ml) was added dropwise at ~ —20°. After 2 hrs. stirring, the excess of chloroform was distilled off at reduced pressure and the residual liquid was extracted with ether which on distillation yielded yellow oily tripropyltin morpholine dithiocarbamate. Yield 70%.

Results and Discussion

Tripropyltin dithiocarbamates have been prepared by the following reaction :—

$$(Pr_3Sn)_2O + 2CS_2 + 2R_2NH \xrightarrow{\sim -20^\circ} 2R_2NC\begin{smallmatrix} \nearrow S \\ \searrow SSnPr_3 \end{smallmatrix} + H_2O$$

The reactions were carried out in an organic solvent such as chloroform, benzene or methanol. The analytical data presented in the Table 1 agree well with the proposed stoichiometry. The compounds are high boiling oily liquids, soluble in common organic solvents such as benzene, methanol, acetone and diethylether. Molecular weight determination by cryoscopic method and electrical conductance studies in absolute methanol indicate that the compounds are monomers and non-electrolytes in solution. They are stable at room temperature.

The infrared spectra have been examined in KBr, nujol and solution and it has been observed that there is neither matrix interaction nor changes in solution. An examination of C – N stretchings in infrared spectra of the compounds at 1465 ±15 cm^{-1}, shows that the absorption is sensitive to the

TABLE—1

ANALYTICAL DATA FOR TRIPROPYLTIN DITHIOCARBAMATES (Pr_3Sndtc)

No.	Compounds dtc.	Mol. Wt. Found (Calcd.)	B.Pt. (°C) at ~1 mm pressure	Analysis % Found (Calcd.)			Absorption frequencies (cm^{-1})	
				Sn	C	H	C–N	C–S
1.	morpholine	380 (410)	170-180	29.06 (29.02)	40.89 (40.98)	7.05 (7.07)	1460 vs 1465 s	1000 vs 1020 s
2.	piperidine	383 (408)	200-205	29.16 (29.17)	44.16 (44.12)	7.58 (7.60)	1449 sd 1460 s	990 1005 } br,s
3.	dibutyl	430 (452)	198-200	26.34 (26.33)	47.72 (47.79)	8.59 (8.63)	1470 sd 1480 s	990 s 1010 w
4.	N-methylaniline	378 (450)	136-38	27.65 (27.67)	47.38 (47.44)	6.76 (6.74)	1455 sd 1460 s	990 s 1005 w
5.	diethyl	372 (396)	—	30.00 (30.05)	42.51 (42.42)	7.86 (7.83)	1481 vs 1460 s	990 1000 } s,br
6.	N-ethylaniline	425 (444)	160-65	26.76 (26.80)	48.69 (48.65)	6.92 (6.98)	1455 s 1460 w	990 s 1020 w

nature of the organic group attached to the nitrogen tom. The substitution of an alkyl group by a heterocyclic group lowers the C – N absorption frequency since the former has high electron releasing capacity while the latter is an electron withdrawing group. The co-ordination behaviour of dithiocarbamate group whether monodentate or bidentate is reflected by C – S stretching absorptions[2]. Presence of two bands at 990 and ($1010 \pm 10\ cm^{-1}$) shows the monodentate character of the dithiocarbamate moiety[1,3].

In the far infrared region, asymm Sn – C and sym Sn – C stretchings have been identified at 590 and 510 cm^{-1} respectively[4,5]. The strong intense absorption band at 370 cm^{-1} is assigned to Sn – S stretching mode of vibration[6].

The proton magnetic resonance spectra recorded in $CDCl_3$ show the presence of two groups of signals, one possessing split signals due to $N-CH_2$ protons at ~ 6-7τ which indicates restricted rotation about C – N bond making the two groups nonequivalent[7] and thus supporting monodentate character of the dithiocarbamate group[8]. The second group of signal has multiplet at 8.2-9.2τ due to alkyl protons. In the case of compounds containing phenyl ring a multiplet is observed at ~2-3.5τ. The spectra and their integration agree well with the proposed stoichiometry.

The observed stoichiometry coupled with the infrared and proton magnetic resonance spectral data suggest an ester type structure for the newly synthesized compounds possessing a monodentate dithiocarbamate moiety and tetra co-ordinated tin atom.

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Cyclic Coagulation of Surface Waters in Laterite Soils

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IN the place of hackneyed coagulants in water treatment, viz., alum and hydrated coppers and of the costlier polymeric analogues, a new coagulant has been found in $MgCO_3$ by Thompson *et.al*[1]. The chief advantage claimed for this coagulant is the absence of sludge disposal problem. It can be regenerated from the sludge thus ensuring cyclic coagulation[2].

TABLE

Sample No.	Amount of $MgCO_3$ (mg/lit)	Amount of $Ca(OH)_2$ (mg/lit)	Before Coagulation				After Coagulation			
			Turbidity	pH	Hardness	Alkalinity	Turbidity	pH	Hardness	Alkalinity
1.	13.3	10.7	39	7.5	32.68	19.89	8	7.7	24.88	29.95
2.	20 75	18.6	42	7.5	30.50	21.32	2	8.0	56.68	52.02
3.	16.60	15.0	28	7.4	62 66	41.31	3	7.8	48.90	49.78
4.	13.30	10.7	31	7.6	56.63	55.09	2	7.9	60.90	64.27

Hardness and Alkalinity in mg/lit. of $CaCO_3$

$MgCO_3$ in the presence of lime is converted into sparingly soluble $Mg(OH)_2$ which takes the fine particles in suspension down with it.

Dosage of $MgCO_3$ required with different characteristics of water have been tabulated[1].

In the present work cyclic coagulation using $MgCO_3$ was tried on surface waters collected from different ponds used exclusively for potable purposes by the public of Karaikudi. The hardness, *p*H, alkalinity as well as turbidity were determined both before and after coagulation for each sample. The dosage of $MgCO_3$ as also the relative amounts of $MgCO_3$ and $Ca(OH)_2$ were optimised so as to reduce the residual turbidity to the minimum possible level without causing an undue increase in hardness or alkalinity. The results are tabulated in the following table.

In each of the cases the *p*H slightly rose up. The *p*H increase helps recarbonation by lessening the amount of CO_2 needed. *p*H and alkalinity do not correspond linearly in the tabulated results. This is to be expected as *p*H is a measure of only H^+ or OH^- concentration while alkalinity takes into account all ions such as OH^-, CO_3^{2-}, HCO_3^- and also free CO_2.

Except with sample no. 2 the hardness has not appreciably changed during coagulation. Karaikudi has laterite soil within a few feet depth and in some regions even on the surface. The composition of the soil also varies within a few metres as gauged by the iron content of the laterite. This fact partly explains the non-conformity of sample No. 2 with others in the context of hardness.

Dosage of $MgCO_3$ is much less than the dosage of alum. The dosage of alum for soft surface waters has been determined by Culp and Culp[3] as 20 mg/1. The samples taken up for investigation in the present work are soft as per specifications laid down by the American Water Works Association in 1968[4]. Thus the sample consumes less of $MgCO_3$ than it would consume alum which is incidently costlier than $MgCO_3$.

The work regarding determination of effective *p*H range for coagulation is under progress.

Experimental

The experimental method followed by us is given in Chemistry for Sanitary Engineers, Sawyer and Mccarty[5]. 300 ml of the sample was taken in a glass jar. Suspensions of $MgCO_3$ (1 ml = 2.5 mg) and $Ca(OH)_2$ (1 ml = 1.8 mg) were prepared. The desired amount of coagulant was added to the sample with vigorous stirring. Then the sample was flocculated for 45 min on a paddle stirrer. The sample was allowed to stand and the clear water was analysed for turbidity, *p*H, hardness and alkalinity. (For turbidity measurements, photo-electric turbidity meter by Toshniwal Instruments, was used).

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Preparation of a Liquid Polysulfide Polymer for Leather Impregnation

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Manuscript received 6 January 1978, accepted 11 April 1978

ONE of the most important industrial leathers viz., oil seal leathers is used for a wide variety of purposes in aeroplanes, automobiles and elsewhere as pneumatic or hydraulic packings that are subjected to high pressures and frictional endurance such as air-brakes and hydraulic rams. These leathers should not harden up in hot oil, must be capable of being moulded so that they retain their shape and flexibility at elevated as well as low temperatures. The main property imparted by the impregnant is resistance to hot air, water and hot oils under high pressure as high as 10.5 Kg/cm^2 and temperatures ranging from 53.9 to 121.1°[1].

The common impregnating agents such as tallow and waxes will not stand these stringent requirements resulting in failure of specimens.

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The right type of impregnating materials developed for such industrial uses are polysulfide liquid polymers such as LP-2, LP-3, LP-8, etc.[4] Processes for preparations of such liquid polymers are covered by patents and the conditions of preparation uncertain.

In the present work, a liquid polysulfide polymer suitable for leather impregnation was obtained by condensation of bis-2-chloroethyl formal and sodium polysulfide[5] and its chemical structure determined.

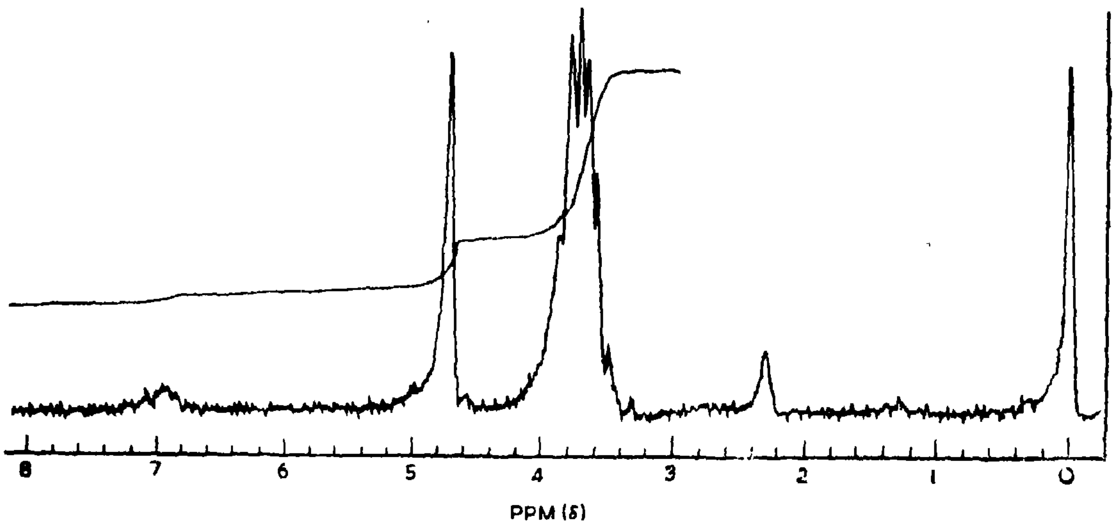
The bis-2-chloroethyl formal was prepared by the condensation of purified and distilled ethylene chlorohydrine(B.P. 125-129°) with 37% formaldehyde(LR B.D.H.) and removing water as an azeotrope with xylene, for 2.5 hours. The formation of the formal proceeds very readily, catalysed by the residual acidity present in chlorohydrin, nearly to completion.

$$2Cl-CH_2-CH_2-OH+CH_2O$$
$$Cl-CH_2-CH_2-O-CH_2-O-CH_2-CH_2-Cl+H_2O$$

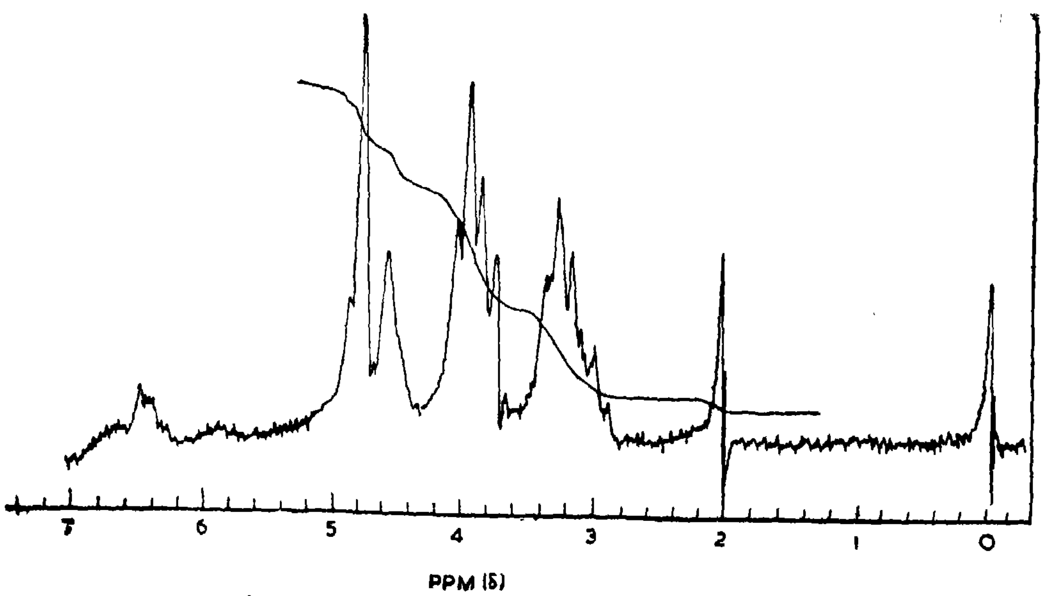
Residual xylene was distilled off under vacuum and the product neutralised with gaseous ammonia.

Sodium sulfide (commercial) was heated in twice the amount of water, cooled and centrifuged. To the heated clear solution, sulfur powder (75% on the weight of sodium sulfide) was added slowly with stirring, heated for 30 minutes and again centrifuged to give sodium polysulfide.

Bis-2-chloroethyl formal was heated over boiling water and sodium polysulfide solution was added slowly with stirring (Bis-2-chloroethyl formal : sodium polysulfide 9 : 10 by weight). 0.1% of tetrachloroethane was also added as a cross-linking agent. 50% of water was added and heating continued.



NMR Spectrum of Bis-2-Chloroethyl formal



NMR SPECTRUM OF EC-1000

After about 25 hours, the initially existed two layers disappeared, forming one layer with sediments. Heating was further continued till a highly viscous pitch settled down, with minimum amount of aqueous layer.

The contents were washed with water to ensure complete removal of sodium chloride and other water soluble products formed.

The polymer layer was then extracted with dichloroethane. Finally dichloroethane was evaporated or distilled off to give a viscous polymer.

The polymer obtained (named EC-1000) thus was very clean and could be stored indefinitely.

The structure of this polymer and its precursor were ascertained by consideration of their spectral properties.

In the infra-red spectrum, bis-2-chloroethyl formal(I), the precursor for EC-1000, shows absorptions at wavelengths given in Table 1. This together with the NMR spectrum where the signals appear at δ 4.67 (s, 2 pr) and two doublets at δ 3.70 and 3.63 ($\delta = 7$ Hz each) provides conclusive evidence for the assigned structure (I).

$$Cl-CH_2-CH_2-O-CH_2-O-CH_2-CH_2-Cl \quad \ldots \quad (I)$$

The spectral data of the polymer are very much similar to those of Thiokol LP-3 (Thiokol Corporation, USA). The details of infra-red absorptions are given in Table 1. In the NMR spectrum, the methylene dioxy group appears as a singlet at δ 4.78, the S–H absorption as a broad singlet between δ 4.40-4.60 (exchangeable with D_2O).

TABLE—1

	Infra-red absorption frequency (wave number cm^{-1})	assignment
Monomer-Bis-2-chloroethyl formal	2780 shoulder	$O-CH_2-O$
	1450 strong	CH_2-O def.
	1470 strong	CH_2-Cl def.
	1370 medium	C–C skeletal
	1290 strong	CH_2 wag
	1155 | strong 1120 | broad	C–O stretch
	745 broad and strong	C–Cl stretch
Polymer EC-1000	2780 medium	$O-CH_2-O$
	1460 strong	CH_2-O def.
	1410 strong	CH_2-S def.
	1370 strong	C–C skeletal
	1280 strong	CH_2 wag
	1155 strong	
	1120 broad	C–O st.
	710 strong	$O-CH_2-O$
	670 broad	C–S st.
	490 broad	S–S st.

The methylene absorptions present quite interesting features. While the methylene protons adjacent to oxygen generate the usual triplet at δ 3.97, the CH_2, α to polysulfide unit appear as a complex pattern situated between δ 2.80-3.40. This diastereotopic nature of these methylene protons points to a strong perturbation by the polysulfide unit in EC-1000 and provide added support for the assigned structure (II), for EC-1000.

$$HS-[CH_2-CH_2-O-CH_2-O-CH_2-CH_2-(S)_x]_n-CH_2-CH_2-O-CH_2-O-CH_2-CH_2-SH \quad \ldots \quad (II)$$

Further work is underway in fully characterising this polymer with respect to molecular weight, etc. Initial results on the application of the polymer on leathers show encouraging results.

Acknowledgement

The authors' thanks are due to Dr. K. Narasimhan, Department of Organic Chemistry, University of Madras, for interpretation of spectral data.

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Gravimetric Determination of Copper(II) with Anilinium Tetraisothiocyanato-dianilinechromate(III)

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IT has been found that tetraisothiocyanatodianiline-chromate(III) anion forms a stable, crystalline and easily filterable compound with copper(II), molecular weight being 1072.62 (gravimetric factor 0.0592).

Experimental

Anilinium tetraisothiocyanatodianilinechromate (III) : The reagent was prepared by the method

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of Ganescu[1]. Freshly prepared saturated solution of the compound in 50% aqueous ethanol was used.

Copper(II) solution : A standard solution of copper(II) was prepared by dissolving copper(II) sulphate (A.R.) in distilled water containing a little sulphuric acid. The metal content was determined by the cuprous thiocyanate method[2].

Diverse ions : Solutions of other ions were prepared from the chloride, nitrate or sulphate salts (A.R.) of cations and the metal contents were determined by conventional and standard methods[2].

Procedure for estimation of copper(II) : To an aliquot of standard solution containing 14-21 mg of copper(II), was added liquor ammonia (1 : 1) in slight excess to obtain a deep blue coloured copper-ammine complex. This solution was filtered (to remove insoluble hydroxides of other metals) and the reagent solution was added dropwise to precipitate out brownish pink coloured complex, $[Cu(NH_3)_4][Cr(NCS)_4(PhNH_2)_2]_2$. The precipitate was kept in an ice bath for 30 min (to avoid any loss due to solubility at room temperature) filtered through a weighed sintered or gooch crucible, washed successively with cold water containing few drops of reagent solution, 10% alcohol and finally with ether. The precipitate was dried at 105-110° to a constant weight. The precipitation is quantitative between *p*H 8.5-10.5 and 14 mg of copper can be successfully estimated with an accuracy of ± 0.33%.

Composition of the complex : The composition of the complex was determined from its analysis for copper, chromium and the isothiocyanate contents (found : Cu, 6.05 : Cr, 9.56 ; NCS, 43.54% Calcd. for $[Cu(NH_3)_4][Cr(NCS)_4(PhNH_2)_2]_2$: Cu, 5.93 ; Cr, 9.70 ; NCS, 43.32%) which correspond to the given formula.

Effect of diverse ions : Estimation of copper(II) can be successfully carried out in the presence of many common cations such as, Li^+, Pb^{2+}, Bi^{3+}, Al^{3+}, Fe^{3+}, Ce^{3+}, Th^{4+}, Mn^{2+}, Ba^{2+} and Mg^{2+}. However, the cations Ag^+, Au^{3+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Ni^{2+}, Pd^{2+}, Pt^{4+}, Rh^{3+}, Ir^{3+}, Ru^{3+} and Os^{4+} interfere in the estimation of copper(II) by this method. Interference by some metals, viz., Bi^{3+}, Al^{3+}, Fe^{3+}, Ce^{3+}, Th^{4+} which form insoluble hydroxide is eliminated by filtration of the hydroxide prior to the precipitation of the complex. A double precipitation had to be done to remove the traces of adsorbed copper complex from the hydroxides.

Acknowledgement

Authors thanks are due to Dr. D. C. Rupainwar, Reader, Dept. of Applied Chemistry, Institute of Technology, B. H. V., Varanasi for going through the manuscript and suggestions. Our thanks are also due to the State C.S.I.R., U.P., Lucknow for financial assistance.

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J. Indian Chem. Soc.
Vol. LV, May 1978, pp. 527

Book Review

Topics in Sulfur Chemistry : Vol. 3. Edited by A. Senning. Publisher : Georg Thieme Stuttgart. 128 Pages.

The book comprises three reviews covering a broad spectrum of sulphur chemistry with valuable information related to applied technology and fundamental chemistry. The publisher has maintained the reputation and tradition of the series.

First chapter by E. J. Goethals gives a systematic and comprehensive picture of facts and trends in the area of sulphur containing polymers. The discussion with vast references in this article will be an important asset to polymer chemists.

Second chapter reviewed by V. Moss and D. A. Nole stresses on the modern trend of application of sulphur in electrical power sources, comprising fuel cell and polar cell and their special applications in powering space vehicles and development of non-polluting electrical cars. The authors have analysed the important practical problems which will inspire any worker in the field.

The last chapter is well presented by G. H. Schmid who has discussed the important and latest developments in the area of thiiranium ions which have wide possibilities to synthetic chemists to steer a course of complicated synthetic sequences.

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Owing to unusual increase in the cost of paper, printing charges and postal rates the Council of the Society has most reluctantly been forced to revise the Annual Subscription Rates (inclusive of postage by Surface Mail) of the Journal of the Indian Chemical Society **with effect from January, 1979** as follows :

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Some Transition Metal Halide Complexes of Cyanoacetylhydrazide

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Metal complexes of cyanoacetylhydrazide (CAH) were prepared. I.R. spectra of the solid complexes, electronic spectra both in solid phase and in solution, are discussed. This bidentate ligand coordinates through the carbonyl oxygen and the cyanide nitrogen groups. The structure of the solid complexes are discussed.

DURING the progress of this work, two studies have appeared. Zommer[1] in their studies on the spectra of cyanoacetylhydrazide of copper(II), have suggested the "imidol" structure. Paul et al[2] in their studies on I. R. spectra of titanium and antimony complexes of cyanoacetylhydrazide suggested only the carbonyl oxygen as the coordination site.

The aim of the present investigation is to ascertain by as much evidence as possible the nature and composition of cyanoacetylhydrazide with some metal ions.

Experimental

Material used :

Cyanoacetylhydrazide was prepared by refluxing ethylcyanoacetate with hydrazine[3]. It was purified by repeated crystallization from ethanol (m.p., 114-115°). All the metal salts used were of AR grade.

Physical measurements :

Spectrophotometric measurements were done in the visible SP. 1800 using 1 cm matched silica and glass cells.

The I.R. spectra of the solid materials were taken in KBr discs using a Pye Unicam SP. 2000 infrared spectrophotometer.

The conductance values were measured using a conductivity cell of the G.M. type dipping in the solution to be titrated, The temperature was adjusted by placing the cell in an ultrathermostat. A Beckman conductivity bridge was employed.

Preparation of the Complexes :

1 : 1 and 1 : 2 metal—ligand complexes were prepared by refluxing equimolar amounts of the hydrazide and the metal salts in absolute ethanol. The solid complexes filtered, washed with ethanol and dried in a vacuum desiccator.

Analysis of the Complexes :

Halides were determined gravimetrically as silver halide, cobalt as cobalttetrapyridinium dithiocyanate. Cadmium, manganese, and zinc were determined volumetrically by EDTA using Eriochrome black T as indicator. Hydrazine nitrogen was determined as described earlier[4].

Results and Discussion

The complexes obtained have the general formula $M(HL)X_2.nH_2O$ (M = Co, Cd, Mn and Zn), X = (Cl, Br), HL = neutral ligand and n = 0 − 3 or $M(HL)_2X_2.nH_2O$(M = Co, Cd and Mn), X = Cl or Br and n = 1 − 3. Analytical data are reported in Table 1. All the complexes are insoluble in various

TABLE 1—ANALYTICAL DATA AND SOME PHYSICAL PROPERTIES OF CYANOACETYLHYDRAZIDE COMPLEXES

Compound	M. P.,	Colour	% Calculated			% Found			Molar Conductance in DMF
			Cl or Br	Metal	N_2H_4	Cl or Br	Metal	N_2H_4	
HL	115	White	–	–	32.34			32.15	
$Co(HL)Cl_2.2H_2O$	185	Pink	22.0	27.3	12.2	22.2	26.8	12.1	11.6
$Co(HL)_2Cl_2.2H_2O$	195	Pink	19.2	17.5	17.4	19.4	16.2	17.6	19.6
$Cd(HL)Br_2.3H_2O$	158	White	28.3	25.7	8.1	27.6	26.4	7.5	30.1
$Cd(HL)_2Br_2.3H_2O$	165	White	31.1	21.5	12.6	30.5	21.4	12.2	30.3
$[Cd(HL)Cl.H_2O]Cl.H_2O$	185	White	22.8	35.6	10.1	22.3	35.3	10.6	140.6
$[Cd(HL)_2Cl.H_2O]Cl$	145	White	17.8	28.4	16.0	18.1	30.1	16.6	140.6
$Mn(HL).Cl_2.H_2O$	above 280	Yellow	21.2	15.6	17.9	20.7	16.1	18.7	23.6
$Mn(HL)_2Cl_2.H_2O$	above 280	Yellow	29.6	22.1	12.6	29.2	22.6	13.2	45.6
$Zn(HL)_2Cl_2$	220	White	19.2	21.2	–	19.5	21.9	–	30.7

HL = Cyanoacetylhydrazide.

common solvents including water and methanol, but easily soluble in DMF.

Electrical conductivity :

The molar conductance values in DMF at the concentration 10^{-3} M exhibits low values of Λ_m support non-electrolytes in DMF, except the cadmium complexes which have the value 140.6 $ohm^{-1}cm^2M^{-1}$, characteristic for 1 : 1 type complex.

The conductometric titration curves were obtained by titration of 10 ml 0.001*M* solutions of Co(II), Cd(II), Mn(II) and Zn(II) against 0.01*M* ligand solution. Curves drawn between conductances of the solutions and the number of ml of cyanoacetylhydrazide solution showed continuous decrease in conductance with successive addition of the ligand. Moreover, the curves exhibited one or more breaks at certain molar ratios of ligand to metal. The position of the break denoted the composition of the complex formed. Representative curve are shown in Figure 1.

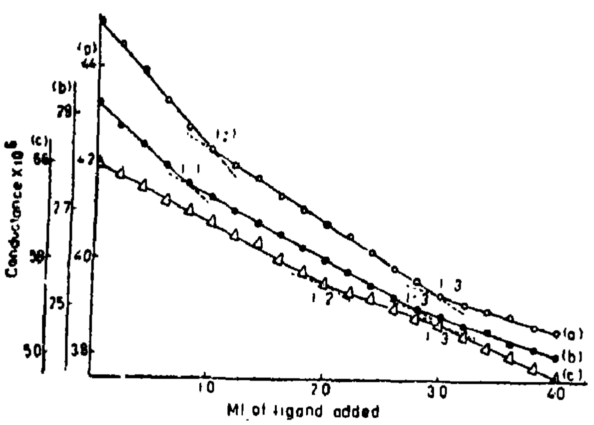


Fig. 1. Conductometric titration curves for (a) $CoCl_2$; (b) $NiCl_2$ and (c) $MnCl_2$ with Cyanoacetylhydrazide

Spectrophotometric studies :

Visible spectra of Co(II) solution shows blue shift of the λ_{max} with increasing concentration of CAH. The stoichiometries of the complex were determined by the methods of Jones[5], Job[6], Asmus[7] and Bent[8] which gave evidence for the formation of stable complex in simple ratio.

Spectrophotometric studies on the complexes of Co(II) with CAH was performed in order to show the possibility of applying the reaction for the micro-determination of Co(II). On plotting the absorbance values vs concentration indicates that Co(II) obeys Beer's law up to $2.4 \times 10^{-3} M$.

The value of the apparent formation constants for Co(II) complex calculated from the molar ratio and continuous variation methods are 3.8×10^4 and 0.57×10^4 respectively. Both methods gave concordant results.

Electronic spectra :

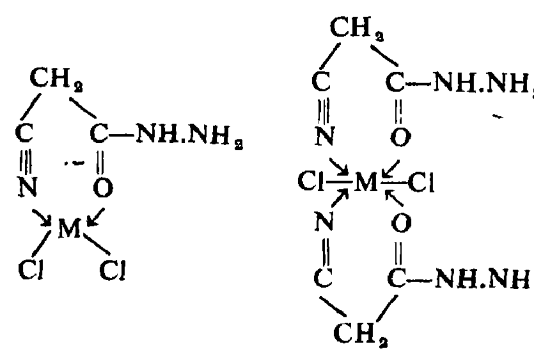
Co(II)-CAH complex shows a band around 500 nm due to the transition $^4T_{1g} \longrightarrow {}^4T_{1g}(P)$ expected for octahedral Co(II) complexes[9]. The electronic spectra of Co(II) complex both in solid phase and in solution are typical of an octahedral stereochemistry.

Infrared Spectra :

The I. R. spectrum of cyanoacetylhydrazide has been discussed by Mashima[10]. The results are provided in Table 2.

ν(C=O) occurring at 1698 cm^{-1} and amide III at 1258 cm^{-1} in the spectrum of cyanoacetylhydrazide are shifted to lower and higher values respectively in the spectra of the complexes. Thus, a negative shift in the carbonyl stretching frequency and a positive shift in amide III band strongly suggest coordination via carbonyl oxygen.

A positive shift in ν(N–H) in the spectra of the complexes indicates that the nitrogen is not involved in coordination. Also, the ν(C≡N) occurring at 2265 cm^{-1} are shifted in all complexes to lower values. It seems that a stable six membered ring with the metal ion and the ligand have taken place. These results indicate a structure of the type I.



I

TABLE 2—ASSIGNMENT OF IMPORTANT FREQUENCIES (cm^{-1}) OF (CAH) AND ITS COMPLEXES

Compound	ν(N–H)	ν(C≡N)	Amide I	Amide II	Amide III
HL	3180 vs, 3020 m, 2970 s	2265 vs	1690 vs	1534 m, 1464 s	1258 m
$Co(HL)Cl_2.2H_2O$	3290 vs, 3230 m, 3150 w	2255 w	1670 s	1570 s	1260 w
$Co(HL)_2Cl_2.2H_2O$	3230 s, 3200 s, 3180 m	2250 m	1670 s	1580 s	1265 m
$Cd(HL)Br_2.3H_2O$	3260 s, 3220 s, 3180 s, 3050 m	2240 s	1670 s	1540 m	1280 w
$Cd(HL)_2Br_2.3H_2O$	3240 s, 3200 s, 3140 s, 3070 m	2260 s	1670 s	1540 m	1270 w
$[Cd(HL)Cl.H_2O]Cl.H_2O$	3260 s, 3180 m, 3140 w, 3100 m	2220 s	1660 s	1540 w	1265 w
$[Cd(HL)_2Cl.H_2O]Cl$	3280 s, 3210 s, 3160 m, 3100 m	2240 s	1670 s	1550 m	1270 m
$Mn(HL)Cl_2.H_2O$	3240 m, 3160 s, 3120 s, 3060 w	2220 m	1660 s	1540 m	1260 w
$Mn(HL)_2Cl_2.H_2O$	3280 s, 3200 m, 3170 s, 3050 m	2240 s	1670 s	1550 s	1270 w

In support of this suggestion we have examined the I.R. spectra of the complexes and have found that N–M frequency of $-C\equiv N\longrightarrow M$ group appears [11] in the region 600–800 cm^{-1}.

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Some New *Trans*-Bis(Dimethylglyoximato)cobalt(III) Complexes Containing Coordinated Azide—Synthesis and Spectra

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Some new azidocobaloximes of the general formula *trans*-$Co(DH)_2LN_3$(DH^- – ^-ON – $C(CH_3)$ – $C(CH_3)$ – N-OH ; L-NH_3, aniline, pyridine or N_3^-) have been synthesized and their i.r and u.v spectra obtained. The u.v. spectra of the conjugate bases of these complexes have also been obtained. A detailed study of the charge-transfer spectra of the complexes and their conjugate bases has been carried out.

RECENT literature on the chemistry of the cobaloximes indicates that not much attention has been paid to the possibility of studying the azidocobaloximes. Such a study should be interesting, in view of the duality of the behaviour of cobalt as a soft acid with dimethylglyoxime and the Schiff bases and as a hard acid with ethylenediamine and related ligands[1]. As part of a study of the equilibria and reactions of nonelectrolytes of the type *trans*-acidoaminebis(dimethylglyoximato)cobalt(III) we have included the cobalt-azide system for investigation[2,3]. This paper reports the synthesis and spectra of diazidobis(dimethylglyoximato)cobaltate(III), and of some *trans*-azidoaminebis(dimethylglyoximato) cobalt(III) systems, where 'amine' represents typical bases like ammonia, pyridine and aniline.

Experimental

Materials : All the chemicals used for the preparations were analytical reagents (BDH). Pyridine and aniline were distilled once before use.

Synthesis : The starting material was $Co(DH)_2(H_2O)Cl$ prepared by the method of Ablov[4].

trans-$Na[Co(DH)_2(N_3)_2].2H_2O$(I) : A solution of sodium azide (5.7 gm, 0.087 mol.) was added to a suspension of [$Co(DH)_2(H_2O)Cl$] (10 gm, 0.029 mol.) in 30 ml of water with stirring for 20-30 minutes. A red-violet solution of diazidobis(dimethylglyoximato)cobaltate(III) was obtained, from which the solid complex separated on cooling at 0-5°. The complex was then filtered, dried and recrystallized from ethanol (yield 50%). Anal: Found : C, 24.51 ; H, 3.62 ; Co, 13.58 per cent. Calcd. for $Na[Co(DH)_2(N_3)_2].2H_2O$; C, 24.25 ; H, 3.56 ; Co, 13.63 per cent.

trans-[$Co(DH)_2(NH_3)N_3$(II) : Ammonia (25%, 0.7 ml, 0.0092 mol.) was added in drops with stirring to a saturated solution of I (2 gm, 0.0046 mol.) containing two drops of glacial acetic acid. Red precipitate of II was formed immediately. The mixture was stirred for 30 mts. and the complex was filtered, washed with alcohol and ether and dried. Recrystallization was done from ethanol (yield 70%). Anal : Found : C, 27.4 ; H, 4.52 ; Co, 16.82 percent. Calcd. for $Co(DH)_2(NH_3)N_3$; C, 27.6, H, 4.92 ; Co, 16.92 per cent.

trans-$Co(DH)_2(py)N_3$(III) : Pyridine (0.7 ml, 0.0092 mol.) was added in drops with stirring to a saturated solution of I (2 gm, 0.0046 mol.) containing two drops of glacial acetic acid. Red precipitate of III was formed immediately. The mixture was stirred for 30 mts and the complex filtered, washed with alcohol and ether and dried. Recrystallization was done from ethanol (yield 80%). Anal : Obsd. : C, 38.31 ; H, 4.51 ; Co, 14.31 per cent. Calcd. for $Co(DH)_2(py)N_3$; C, 38.05 ; H, 4.66 ; Co, 14.36 per cent.

trans-[$Co(DH)_2$(aniline)N_3] (IV) : An alcoholic solution of aniline (0.80 ml, 0.009 mol) was added in drops with stirring to a saturated solution of I (2 gm, 0.0046 mol) in the presence of two drops of glacial acetic acid. Shiny, pale red precipitate of IV was formed immediately. The mixture was stirred for fifteen minutes, washed with alcohol and ether and dried. Recrystallization was done from ethanol (yield 80%). Anal : Found : C, 39.49 ; H, 4.89 ; Co, 13.75 per cent. Calcd. for $Co(DH)_2$-(aniline)N_3 : C, 39.62 ; H, 4.98 ; Co, 13.88 per cent.

Spectra : The infrared spectra were recorded in KBr disks with Perkin-Elmer 337 IR spectrophotometer. The u.v and visible spectra were recorded in 10 vol. % ethanol with a Beckman DK-2A recording spectrophotometer.

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Results and Discussion

The nonelectrolyte complexes of the type *trans*-$Co(DH)_2LN_3$ were prepared by treatment of the base L(pyridine, ammonia or aniline) with $[Co(DH)_2(N_3)_2]^-$. The complexes were assigned a *trans*-configuration on the basis of the δ_{OH} observed at 1740-50 cm^{-1} in the i.r spectra of these complexes (Table 1)[6]. In alkaline solution the proton involved in hydrogen-bonding is removed in a rapid reversible reaction[2]

TABLE 1—INFRARED ABSORPTION FREQUENCIES OF THE AZIDOCOBALOXIMES(III) IN CM^{-1}

Complex	N_3		DMG			
	ν_{asym}	ν_{sym}	δ_{OH}	$\nu_{C=N}$	ν_{NO}	
$Co(DH)_2(N_3)_2$	2016 2036	1296	1742	1581	1086	1223
$Co(DH)_2(NH_3)N_3$	2024	1296	1749	1570	1078	1231
$Co(DH)_2(an)N_3$	2030	1292	1740	1575	1088	1232
$Co(DH)_2(py)N_3$	2016	1276	1718	1560	1090	1231

$$[Co(DH)_2LN_3]+OH^- \rightleftharpoons [Co(D_2H)LN_3]^- + H_2O$$

The infrared absorption spectra (4000-400 cm^{-1}) of the complexes were obtained in KBr disks. Table 1 shows the important i.r frequencies of the coordinated azide and dimethylglyoxime. The frequencies characteristic of coordinated NH_3, pyridine and aniline were observed. The intense absorption at 2010-2040 cm^{-1} is due to the azide asymmetric stretch[8] while the weaker absorptions at 1270-1290 cm^{-1} are due to the symmetric stretching vibrations of the coordinated azide (ν_{sym}).

U. V. and Visible Spectra : Table 2 shows the characteristic u.v. and visible absorption maxima and the corresponding assignments for the azidocobaloximes. The ligand field spectra of the complexes show one band at 470-490 nm for the nonelectrolytes and at 540 nm for $[Co(DH)_2(N_3)_2]^-$ which may be assigned to the spin-allowed $^1A_{1g} \longrightarrow {}^1T_{1g}$ transition[7] with the other spin-allowed $^1A_{1g} \longrightarrow {}^1T_{2g}$ band masked by the intense charge-transfer bands. The positions of the maxima correspond to the following order of the spectrochemical series :

$NH_3 > py > An > N_3^-$, consistent with previous results[8]. The weak field of N_3^- arises out of the destabilization of the t_{2g} orbitals due to π-interactions from N_3^-.

The CT spectra (Fig. 1, Table 2) of the *trans*-$[Co(DH)_2N_3L]$ complexes show maxima mainly centred at 245-250 nm and 295-335 nm. $[Co(DH)_2(NH_3)N_3]$ and $[Co(DH)_2(py)N_3]$ show maxima at 298 nm and 305 nm respectively while very broad bands are observed at 330 nm and 332 nm for $Co(DH)_2(aniline)N_3$ and $Co(DH)_2(N_3)_2^-$ respectively, the order roughly parallelling the ligand field maxima. Studies of the CT spectra of the cobaloximes have also been made by Yamano *et al*[9] who assign the 245 nm band to intra-ligand π-π^* transitions in the coordinated dimethylglyoxime. In their studies with a $Co(DH)_2(X\text{-}py)_2^+$ series (X-py = substituted pyridines), Yamano *et al*[9] have observed two bands, 315-370 nm (py→Co, LMCT) and 275-305 nm ($d\pi(Co) \rightarrow \pi^*(DMG)$, MLCT). One would also expect to observe maxima due to $\sigma(DMG) \rightarrow \sigma^*(Co)$ LMCT which generally appears as a shoulder at 360-380 nm[10] in the $Co(DH)_2$ systems, with a lower intensity compared to the 300 nm bands and is masked in the spectra of the azidocobaloximes by the intense short wavelength bands. Another absorption masked here is the intra-ligand CT absorption in N_3^-, expected at 300-350 nm[11].

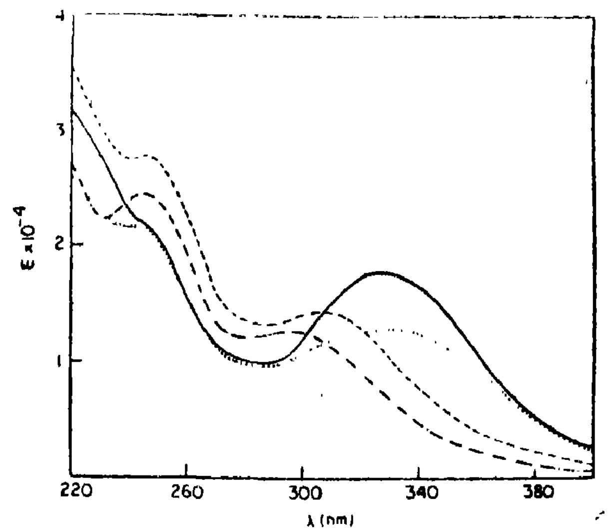


Fig. 1. U.V. Spectra of the azidocobaloximes(III)
--------$Co(DH)_2(py)N_3$, -.-.-.-.-.-. $Co(DH)_2(NH_3)N_3$, ... $Co(DH)_2(an)N_3$, ———— $Co(DH)_2(N_3)_2^-$
Temp : 30° ; $[HClO_4]$ = 0.1 *M*

TABLE 2—ELECTRONIC ABSORPTION MAXIMA (NM) OF THE AZIDOCOBALOXIMES(III)

Complex	$^1A_{1g} \rightarrow {}^1T_{1g}$	$\sigma_L - e_g^*$	$d\pi(t_{2g}) \rightarrow \pi^*$	$\pi - \pi^*$
$Co(DH)_2(NH_3)N_3$	483 (2.47)[a]		295 (4.11)	246 (4.39)
$Co(DH)_2(py)N_3$	485 (2.51)		308 (4.15)	246 (4.45)
$Co(DH)_2(an)N_3$	495 (2.70)		330 (4.16)	247 (4.27)
$Co(DH)_2(N_3)_2^-$	540 (2.58)		331 (4.18)	246[b] (4.27)
$Co(D_2H)(NH_3)N_3^-$		365[b] (3.60)	285 (4.43)	260 (4.60)
$Co(D_2H)(py)N_3^-$		370[b] (3.60)	288 (4.43)	260 (4.56)
$Co(D_2H)(an)N_3^-$		381[b] (3.59)	288 (4.36)	260 (4.55)
$Co(D_2H)(N_3)_2^{2-}$		380[b] (3.62)	280[b] (4.38)	258 (4.53)

[a] log ε in parenthesis , [b] shoulder

The CT spectra of the conjugate bases, obtained by adding alkali to aqueous solutions of the complexes, are also given in Table 2 (Fig. 2). New

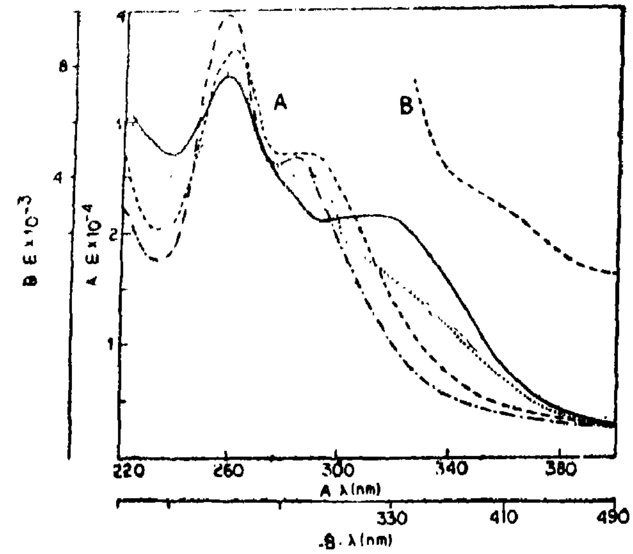


Fig. 2. U.V. Spectra of the azidocobaloximes(III) in alkaline solution :

- - - - - - - - - $[Co(D_2H)(py)N_3^-]$, $[OH^-] = 0.05$ *M*
-·-·-·-·-·- $[Co(D_2H)(NH_3)N_3]^-$, $[OH^-] = 0.5$ *M*
··········· $[Co(D_2H)(aniline)N_3]^-$, $[OH^-] = 0.5$ *M*
———— $[Co(D_2H)(N_3)_2]^-$, $[OH^-] = 3$ *M*

bands may now be observed at 260 nm, 285 nm and 370-380 nm (shoulders) for all the four complexes and at 320-330 nm (shoulders) for $[Co(D_2H)(N_3)_2]^{2-}$ and $[Co(D_2H)(an)N_3]^-$. The 260 nm bands are due to a red shift of the 245 nm bands of the acid solutions of these complexes. What were apparently single bands in $[Co(DH)_2(N_3)_2]^-$ and $[Co(DH)_2(an)N_3]$ have now been split into two, one at 285 nm and the other at Ca. 320 nm (shoulder). The 285 nm bands appear almost unchanged in all the four complexes and are clearly MLCT bands due to transitions of the type $d\pi\ (t_{2g}) \rightarrow \pi^*$ (DMG). The π^*-orbital on the donor nitrogen (DMG) atom in the conjugate bases would be at a higher energy level than the respective acid forms and a $d\pi - \pi^*$ MLCT transition would clearly be blue-shifted in the conjugate-base. The shoulders at 370-380 nm could be assigned to $\sigma(DMG) \rightarrow \sigma^*$ LMCT transitions. These transitions in the spectra of the acid-forms were obviously masked by the more intense bands at shorter wavelengths and are now red-shifted.

The CT spectrum of $Co(DH)_2(N_3)_2^-$ in alkaline solution shows an intense absorption at 330 nm and $Co(D_2H)(an)N_3^-$ also shows a shoulder at this wavelength. These bands are obviously much less affected by *p*H than the MLCT bands mentioned above. In the diazido-complex this band may be assigned to a $(N_3^-)\sigma \rightarrow \sigma^*(d_{z^2})$ LMCT transition while in $Co(D_2H)(an)N_3^-$ a $(an)\sigma \rightarrow \sigma^*(d_{z^2})$ LMCT may give this band. On this scale, LMCT bands corresponding to transitions from NH_3 or py to metal would be expected to occur at shorter wavelengths. The occurrence of the aniline→metal LMCT band at a longer wavelength is also in accordance with the trend in ionization potentials. Accordingly the highest filled MO in aniline is at a higher energy level than the corresponding MO's in NH_3 and py and this trend should be reflected in the position of the LMCT bands arising from transitions from these MO's.

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Studies on Complexes of Isoquinoline with Cobalt(II) and Nickel(II) Alkanoates

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A number of metal complexes of the type $M(O_2CR)_2(IQ)_2$ (where M=Co(II) ; R=H−, CH_3−, C_2H_5−, n- and iso-C_3H_7− and C_4H_9− and M=Ni(II) ; R=CH_3− and C_2H_5− and IQ=Isoquinoline) have been isolated by treating the appropriate metal(II) alkanoate with a large excess of isoquinoline in chloroform and are characterized by magnetic and spectral studies which show that the complexes possess a trans octahedral structure containing bidentate chelating carboxylate groups.

COBALT(II) and nickel(II) acetates are known to form a number of addition complexes[1-5] with heterocyclic ligands like pyridines, quinoline, morpholine, piperidine, piperazine and N-methylpyrazine which have been shown to be 6-coordinated octahedral monomeric complexes excepting quinoline adduct of nickel(II) acetate which has a polymeric structure. Some complexes of cobalt(II) and nickel(II) alkanoates derived from propionic, n- and iso-butyric and n-valeric acids with pyridine have also been prepared[6]. Since no structural studies have been done on these complexes, it was considered interesting to prepare some more complexes of cobalt(II) and nickel(II) alkanoates with a related ligand like isoquinoline and to investigate their structure by magnetic and spectroscopic methods.

Experimental

Cobalt(II) and nickel(II) alkanoates were prepared by published methods[6]. Isoquinoline was fractionally distilled over KOH pellets. Solvents were purified by conventional methods.

Preparation of Complexes : Complexes were prepared by treating a suspension of the appropriate metal(II) alkanoate in chloroform with a large excess of the ligand under reflux for half an hour. The resulting clear solution was filtered and excess of the solvent was removed under reduced pressure. The remaining viscous liquid on keeping for 24 hr over concentrated sulphuric acid in a vacuum desiccator gave a coloured crystalline compound which was recrystallized from methanol and dried over phosphorus pentoxide in vacuum at room temperature.

Cobalt in these complexes was estimated as tetrapyridinedithiocyanato-cobalt(II) and nickel as bis(dimethylglyoximato)-nickel(II). Carbon and hydrogen analyses were carried out in the micro-analytical laboratory of this department.

Magnetic moments were determined by Gouy's method using $Hg[Co(NCS)_4]$ as calibrant. Electronic spectra were recorded in benzene on Beckmann DU-2 Spectrophotometer over the range 360-1250 nm. Infrared spectra were recorded on Perkin-Elmer models 337 and 621. The analytical, molecular weight and magnetic data of the complexes prepared are presented in Table 1 while infrared and electronic spectra are cited in Table 2.

TABLE—1 : ANALYTICAL, MOLECULAR AND MAGNETIC DATA OF COMPLEXES OF ISOQUINOLINE WITH COBALT(II) AND NICKEL(II) ALKANOATES

Sl. No	Compound	Colour	Metal (%)		Carbon (%)		Hydrogen (%)		M. Wt		μ_{eff}
			Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	B.M.
1.	$Co(formate)_2(IQ)_2$	Pink	14.29	14.47	58.58	58.92	3.67	3.92	–	407	4.87
2.	$Co(acetate)_2(IQ)_2$	Pink	13.27	13.54	60.38	60.63	4.48	4.59	413	435	4.89
3.	$Co(propionate)_2(IQ)_2$	Red	12.56	12.72	61.86	62.15	5.02	5.17	452	463	4.93
4.	$Co(n\text{-}butyrate)_2(IQ)_2$	Red	11.78	11.99	63.41	63.49	5.32	5.69	502	491	4.94
5.	$Co(iso\text{-}butyrate)_2(IQ)_2$	Red	11.71	11.99	63.62	63.49	5.38	5.69	480	491	4.89
6.	$Co(n\text{-}valerate)_2(IQ)_2$	Red	11.04	11.34	64.71	64.69	5.94	6.15	–	519	4.94
7.	$Co(iso\text{-}valerate)_2(IQ)_2$	Red	11.13	11.34	64.65	64.69	5.87	6.15	–	519	4.98
8.	$Ni(acetate)_2(IQ)_2$	Light blue	13.14	13.49	59.95	60.87	5.38	5.59	402	435	3.18
9.	$Ni(propionate)_2(IQ)_2$	Light blue	12.61	12.68	62.03	62.19	4.98	5.18	421	463	3.20

TABLE—2 : IMPORTANT INFRARED ABSORPTION FREQUENCIES (cm^{-1}) AND ELECTRONIC SPECTRA (nm) (ϵ) OF COMPLEXES OF ISOQUINOLINE WITH COBALT(II) AND NICKEL(II) ALKANOATES

Compound*		ν(C=C and C=N)				ν(COO) Asym.	ν(COO) Sym.	Δ	ν(O – M)	ν(N – M)	$\lambda_{max}(\epsilon)$		
Isoquinoline	1630	1590	1500	1465	1440	–	–	–	–	–		–	
1.	1640 sh	1595	1510	1470	–	1615	1420	195	265 283	218		–	
2.	–	1610	1510	1468	–	1625	1418	207	270	225	492 sh,	527(48),	1175(7)
3.	–	1595	1500	1465	1445	1630	1421	209	273	212	490 sh,	505(45),	1156(6)
4.	1640 sh	1600	1520	1473	1445	1635	1431	204	288 292	215	487 sh,	502(88),	1160(6)
5.	–	1610	1515	1470	1445	1628	1410	218	285	215	483 sh,	520(35),	1181(7)
6.	1640 sh	1608	1520	1468	–	1625	1421	204	260 285	218	486 sh,	515(47),	1156(8)
7.	1635 sh	1609	1509	1475	–	1627	1416	211	275	218	490 sh,	510(30),	1160(6)
8.	1638 sh	1610	1520	1463	–	1631	1420	211	282	210	385(15),	630(9),	1035(3)
9.	–	1610	1505	1465	–	1633	1420	213	280	212	375(11),	642(7),	1038(4)

*Number refers to compounds in Table 1.

Results and Discussion

The analytical data (Table 1) indicate that complexes are of 1 : 2 stoichiometry of formula $M(O_2CR)_2(IQ)_2$. The complexes are generally soluble in common organic solvents and are quite stable in air. However, iso-quinoline complex of cobalt(II) formate is insoluble in nature. Cobalt complexes are pink or red in colour while nickel complexes are light blue in colour. Molar conductance of $10^{-3}M$ solutions of these complexes in nitrobenzene is below 2 $ohm^{-1}cm^2mole^{-1}$ which suggest that complexes are non-electrolytes[7]. Molecular weights indicate that the complexes are monomeric in solution. Magnetic moment values for cobalt complexes fall in the range 4.87-4.98 B.M. and for nickel complexes in the range 3.18-3.20 B.M. which point that the complexes are high spin and have octahedral stereochemistry. The electronic spectra of cobalt complexes show two main absorption bands around 1175 and 500 nm as expected for octahedral symmetry and may be assigned to $^4T_{1g} \rightarrow {}^4T_{2g}$ and $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transitions respectively. The nickel complexes exhibited the usual three main bands characteristic of octahedral complexes around 1035, 630 and 385 nm and are assigned to $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ electronic transitions. Low values of molar extinction coefficients (ϵCa. 47 l. $mole^{-1}cm^{-1}$) suggest that the complexes are of trans octahedral configuration[8].

Infrared spectra of the complexes show similar features indicating that all the complexes are isostructural. The bands due to C=C and C=N stretching frequencies of the isoquinoline ligand are shifted to higher frequencies indicating the coordination of the ligand through its nitrogen atom in agreement with the observations made by previous workers[9]. The asymmetric (COO) stretching frequencies fall in the range 1635-1615 cm^{-1} while symmetric (COO) stretching frequencies occur in the range 1431-1410 cm^{-1}. The difference between asymmetric and symmetric (COO) stretching frequencies, Δ, in the complexes works out to be around 200 cm^{-1} which falls in the same range as observed for some pyridine[10] complexes of cobalt(II) acetate and propionate which contain bidentate chelating carboxylate group. This suggests that mode of bonding of the alkanoate group in the present complexes is also bidentate chelating. The bands observed in the region 292-260 and 225-210 cm^{-1} have been tentatively assigned to ν_{M-O} and ν_{M-N} vibrations analogous to ν_{M-O} and ν_{M-N} stretching vibrations of amine-metal(II) trifluoroacetate[11] which fall in the region 325-235 and 228-195 cm^{-1} respectively.

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Metal Complexes of Thiopolycarboxylic Acid Co(II), Ni(II), Cu(II) and Cr(III) Complexes with 3,3′-Thiodipropionic Acid

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3, 3′-Thiodipropionic acid forms 1 : 1 coloured complexes with Co(II), Ni(II), Cu(II) and Cr(III) $[M_2L_2]$ and their structures have been characterized on the basis of elemental analysis, magnetic measurements, Infrared and electronic spectral studies. It was found that all these complexes are high spin octahedral. Cobalt(II) and Nickel(II) complexes show normal magnetic moments but copper(II) and Cr(III) show anomalous magnetic behaviour.

METAL complexes of thiopolycarboxylic acids have been the subject of many recent studies[1-5]. Suzuki et. al.[6] determined the stability constants of some metal chelates with 3, 3′-thiodipropionic acid and reported 1: 1 complexes with six membered ring. 3, 3′-Thiodipropionic acid has two carboxylic groups, and one sulphur atom as donors and hence capable to afford the examples of homonuclear metal-metal interaction[7]. The present communication deals with the preparation and characterisation of metal complexes of Cobalt(II), Nickel(II), Copper(II) and Chromium(III) with 3, 3′-thiodipropionic acid $[S(CH_2.\ CH_2.COOH)_2]$.

Experimental

3,3′-Thiodipropionic acid (Evans Chemetics, Inc., New York) of 98.8% was used as such without further purification. All other chemicals used were of A. R. grade.

Preparation of Complexes : The metal complexes of Co(II), Ni(II), Cu(II) and Cr(III) with 3, 3′-thiodipropionic acid were prepared by the general method described here. A solution of hydrated metal chloride (75 ml, 0.2 *M*) was added to an equimolar solution (75 ml and 115 ml in case of Cr(III) complex) in distilled alcohol. A few drops of concentrated NaOH were added and resulting mixture was refluxed for four hours, over steam bath. In case of Cu(II) and Cr(III), a sky blue and bluish green complexes were obtained respectively but in case of Cobalt(II) and Nickel(II), the resulting mixture was concentrated to 50 ml which yield light pinkish and light greenish complexes respectively on refrigeration for two days. The complexes so formed were filtered, washed with alcohol, acetone and ether and dried in vacuo over calcium chloride.

Physical Measurements : The instruments and methods have been given previously[4].

Results and Discussion

3, 3′-Thiodipropionic acid forms 1 : 1 coloured complexes with Co(II), Ni(II) and Cu(II) which are slightly soluble in water and common organic solvents. However Cr(III) complex is almost insoluble in H_2O and common organic solvents. The decomposition temperatures which range between 150-200° show that complexes are thermally quite stable. The molar conductance in D.M.S.O. indicates non-electrolytic nature of these complexes (2.06-3.10 $ohm^{-1}\ cm^{-2}\ mole^{-1}$).

Cobalt(II) Thiodipropionate : The observed magnetic moment 4.92 B.M. of Co(II) thiodipropionate is within the usual range of reported data for high spin octahedral complexes[8] and suggests octahedral symmetry. The diffuse reflectance spectrum shows three absorption bands at 7.52, 16.25 and 19.60 *kk* which are similar to the transitions of octahedral symmetry in Cobalt(II) complexes and further supports octahedral symmetry. The observed ν_2 transition at 16.25 *kK* which is approximately twice but not greater than 2.2 times to that of ν_1 transition (7.52 *kK*) also indicates that the complex is regular octahedral ($\nu_2/\nu_1 = 2.16$)[9]. Thus magnetic and spectral data suggest octahedral symmetry of the complex. Since ligand has only five donor atoms, the sixth coordination site should be completed by sharing a non-bonded oxygen atom with neighbouring molecule forming a dimer as suggested from molecular weight determination (experimental M = 465). A value of β, 0.901 suggests low degree of covalency.

Nickel(II) Thiodipropionate-Monohydrate : It shows magnetic moment 3.27 B.M. and suggests high spin octahedral symmetry. The octahedral stereochemistry is further supported by diffuse reflectance spectrum which shows three bands at 7.50, 14.25 and 23.92 *kK*. The observed separation of ν_2 and ν_1 transition, 9.67 *kK* being considerably lower than the calculated value of 11.28 *kK* for regular octahedral symmetry[10], suggests that the complex is distorted octahedral. This is further supported by ν_2/ν_1 ratio 1.90. The 7.1% decrease in weight at 134° in T.G.A of Nickel complex indicates coordination through a molecule of water. A value at β, 0.935 indicates low degree of covalency.

TABLE 1—ELEMENTAL ANALYSIS, MAGNETIC MOMENTS AND DIFFUSE REFLECTANCE SPECTRAL DATA

Complex	C%		H%		S%		Metal %		Magnetic moment	Transition bands in reflectance spectrum
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found		
$[Co(C_6H_8O_4S)]_2$	30.61	30.56	3.42	3.44	13.60	13.58	25.04	25.10	4.92	7.52, 16.25, 19.60 *kK*
$[Ni(C_6H_8O_4S).H_2O]$	28.49	28.50	3.98	4.00	12.67	12.64	23.21	23.24	3.27	7.50, 14.25, 23.92 *kK*
$[Cu(C_6H_8O_4S)]_2$	30.02	30.14	3.87	3.86	13.34	13.32	26.40	26.42	1.31	14.70, 26.31 *kK*
$[Cr_2(C_6H_8O_4S)_3]$	34.17	34.20	3.78	3.84	15.18	15.16	16.45	16.50	3.26	17.46, 24.52 *kK*

TABLE 2—INFRARED SPECTRAL BANDS OF 3, 3′-THIODIPROPIONIC ACID AND ITS COMPLEXES*

Complex	ν(OH) of H_2O	ν(OH) of COOH	ν_{as} (COO)	ν_s (COO)	ν(C−S)
$C_6H_{10}O_4S$	–	3100, S. Br.	1710 (S)	1430 (S)	730 (m)
$[Co(C_6H_8O_4S)]_2$	–	–	1585 (S)	1405 (S)	720 (m)
$[Ni(C_6H_8O_4S)]H_2O$	3370	–	1580 (S)	1415 (S)	705 (m)
$[Cu(C_6H_8O_4S)]_2$	–	–	1600 (S)	1410 (S)	700 (m)
$[Cr_2(C_6H_8O_4S)_3]$	–	–	1620 (S)	1400 (S)	725 (m)

* All data are in cm^{-1}, S=Sharp, m=medium, br=broad.

Cu(II) Thiodipropionate : The observed magnetic moment value 1.31 B.M. is subnormal in case of Cu(II)-thiodipropionate and suggests spin-spin coupling between unpaired electrons of neighbouring copper atoms. The diffuse reflectance spectrum shows two transition bands at 14.70 *kK* and 26.31 *kK* indicating octahedral symmetry[11] and dimeric nature of the complex.[12] The copper(II) complex will be distorted octahedral due to John Teller effect. Thus in copper(II)octahedral complex, metal ion is penta-coordinated by the ligand and the remaining sixth coordination position will be occupied by Cu–Cu bond forming a dimer. This is supported by magnetic, I.R., diffuse reflectance spectral data and molecular weight determination which comes out to be 468.

Cr(III) Thiodipropionate : The observed magnetic moment value 3.26 B.M. is considerably lower than the spin only value as well as reported data for octahedral complexes and suggests inter or intra molecular antiferromagnetism between Cr(III) ions. The diffuse reflectance spectrum shows two strong bands at 17.46 and 24.52 *kK*, suggesting octahedral symmetry. Thus Cr(III) complex is high spin octahedral in which metal-metal interaction between chromium ions form a polymeric structure.

I.R. Spectra : Infrared spectrum of 3,3′-thiodipropionic acid and its complexes were recorded in the region of 4000-200 cm^{-1}. Disappearance of ν(OH) vibrations and shift in ν_{as}(COO) vibrations[13,14] towards lower wave number in complexes indicate coordination through both bonded and non-bonded oxygen atoms of the carboxylic groups. The C–S stretching frequency shifted towards lower wave number in complexes with respect to free ligand, indicating coordination through sulphur. Thus ligand acts as pentadentate in all the metal complexes forming a six numbered ring with the metal ion, as the non-bonded oxygen atoms are supplied from neighbouring molecule.

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Formation Constants of Mixed-Ligand Complexes of Oxovanadium(IV) with Some Dicarboxylic Acids and Pyridine-2-aldoxime

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Oxovanadium(IV) has been shown to form mixed-ligand complexes, MAL and MAL(OH) (where $M=VO^{2+}$; H_2A = oxalic, phthalic and maleic acids and HL = pyridine-2-aldoxime) from the pH-metric titration curves in the ternary systems, VO^{2+}-dicarboxylic acids-pyridine-2-aldoxime. The formation constants of the mixed-ligand complexes, MAL have been determined at 30±0.5° (μ=0.1 KNO_3).

PYRIDINE-2-aldoxime has been shown in the recent past[1] to form only monohydroxo derivative, VO(OH)A with oxovanadium(IV) by *p*H-metric method and the equilibrium constant for the reaction $VO^{2+}+H_2A^{+}+H_2O \rightleftharpoons VO(OH)A+3H^{+}$ (where H_2A^{+} = pyridine-2-aldoxime hydrochloride) reported. The formation constants of the resulting complexes in the simple binary systems, VO^{2+}-oxalic acid/phthalic acid/maleic acid and ternary complexes with oxalic, phthalic and maleic acids as one of the ligands have also been reported[2-4,6]. Such studies have now been extended to other ternary systems, VO^{2+}-oxalic acid/phthalic acid/maleic acid – pyridine-2-aldoxime and the results are presented in this paper.

Experimental

A stock solution of vanadyl sulphate(BDH) was prepared in doubly distilled water and standardized against disodium salt of ethylenediaminetetraacetic acid using 7-phenylazo-8-hydroxyquinoline-5-sulphonic acid as an indicator[5]. Pyridine-2-aldoxime (Fluka purum), oxalic (BDH AnalaR), phthalic (BDH), maleic (Burgoyne) acids were prepared by direct weighing and standardized potentiometrically against potassium hydroxide (0.1*M*). The *p*H-titrations were carried out at 30± 0.5° with a Cambridge *p*H-meter standardized against 0.05*M* solution of potassium hydrogen phthalate. The volume of solutions to be titrated was always kept constant (50 ml) by mixing with the requisite volume of doubly distilled water; the ionic strength was maintained constant (μ=0.1KNO_3) by adding 5.0 ml of 1.0 *M* KNO_3 to each solution and titrated against standard KOH solution.

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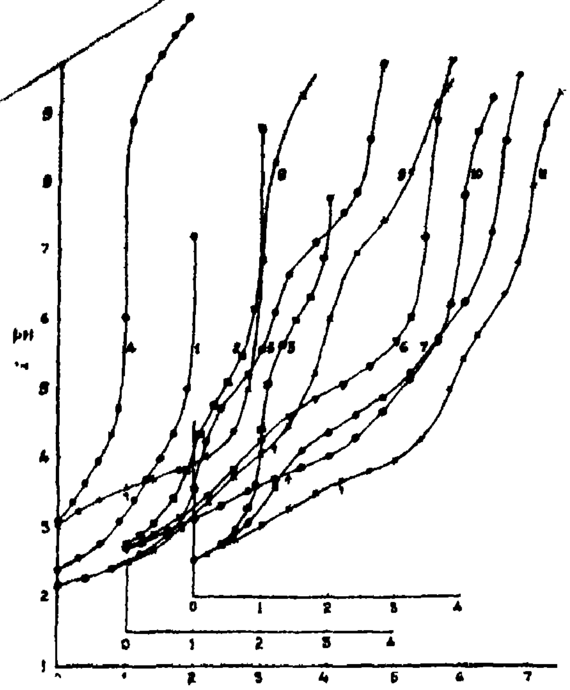
Results and Discussion

The potentiometric titration curves of oxalic, phthalic and maleic acids; pyridine-2-aldoxime and vanadyl sulphate in presence of an equimolar concentration of these ligands have been described earlier[6,1] and the calculations of the acid dissociation constants (k_1 and k_2) of ligands; equilibrium (K_1) and stability (K_{MA}) constants of 1 : 1 chelates and hydrolysis constants of monohydroxo derivatives of 1 : 1 chelates have also been reported (Table 1).

TABLE 1—DISSOCIATION CONSTANTS OF LIGANDS AND EQUILIBRIUM, FORMATION AND HYDROLYSIS CONSTANTS OF 1 : 1 CHELATES (t=30°)

Ligand	pk_1	pk_2	$-\log K_1$	$\log K_{MA}$	$-\log K_H$
Oxalic acid	1.66	3.90	0.91	4.65	4.49
Phthalic acid	2.89	5.04	3.92	4.01	8.47
Maleic acid	2.23	5.97	3.79	4.41	8.58
Pyridine-2-aldoxime	3.73	9.84	–	–	8.40

Curves 9-11 (Fig. 1) represent the potentiometric titrations of vanadyl sulphate in presence of equimolar concentrations of one of the primary ligands (H_2A=oxalic, phthalic and maleic acids) and pyridine-2-aldoxime (H_2L^{+}). In the initial stage, all these curves superimpose over the corresponding 1 : 1 VO^{2+}-oxalic acid/phthalic acid/maleic acid systems (curves 5-7; Fig. 1) and the lowering of these curves, which is a measure of mixed-ligand chelate formation, accurs after m=1.2, 0.2 and 0.4 in case of VO^{2+}-oxalic acid/phthalic acid/maleic acid – pyridine-2-aldoxime systems (m represents the moles of base added per mole of



m = moles of base added per mole of metal ion→

Fig. 1. Potentiometric titration curves of mixed-ligand chelates ; VO(IV)-Oxalic acid/phthalic acid/maliec acid-pyridine-2-aldoxime : 1, Oxalic acid ; 2, Phthalic acid ; 3, Maleic acid ; 4, Pyridine-2-aldoxime ; 5, 6, 7 & 8, VO(IV)-Oxalic acid/Phthalic acid/Maleic acid/Pyridine-2-aldoxime (1 : 1) ; 9, 10 & 11 VO(IV)-Oxalic acid/Phthalic acid/Maleic acid-Pyridine-2-aldoxime (1 : 1 : 1). Arrow indicates the appearance of solid phase.

metal or ligand ions). This indicates that initially a VO^{2+}-oxalic acid, phthalic acid or maleic acid (1 : 1) complex is formed in the above systems. Further, the lowering of these curves in comparison to the corresponding composite curves (which can be drawn by adding the horizontal distance of the secondary ligand curve to the horizontal distance of the VO^{2+}-oxalic acid/phthalic acid/maleic acid curve at the same pH) inferred the formation of mixed-ligand chelates in the ternary systems. Thus the formation of the ternary complexes takes place in overlapping steps and through the formation of 1 : 1 chelates with primary ligands.

Further, poor inflections at $m=4$ followed by another inflection at $m=5$ in case of VO^{2+}-oxalic acid/maleic acid-pyridine-2-aldoxime and only one inflection at $m=5$ in case of VO^{2+}-phthalic acid-pyridine-2-aldoxime indicate the formation of 1 : 1 : 1 mixed-ligand chelate species, $VOAL^-$ and its conversion into hydroxo derivatives in overlapping steps. The formation of ternary chelates is also supported by the analysis of the potentiometric data given below :

Assuming the absence of the species $VOAL_2^{3-}$, $VOAL_3^{5-}$, etc., when the ratio of metal ion to ligands is 1 : 1 : 1 and the formation of only mononuclear metal chelate species, the equilibria involved in the formation of 1 : 1 : 1 mixed-ligand complexes in the above systems, may be represented as :

$$VOA + H_2L^+ \rightleftharpoons VOAL^- + 2H^+ \quad \ldots \text{(i)}$$

and the overall reaction for the formation of the mixed-ligand chelate may be shown as :

$$VO^{2+} + H_2A + H_2L^+ \rightleftharpoons VOAL^- + 4H^+ \quad \ldots \text{(ii)}$$

In the pH-range studied before the precipitation starts, neglecting the concentration of OH^-, L^- and hydrolized species of vanadyl ions as compared with those of other species present in the equilibrium mixture, the following equations are obtained for maintaining the material balance :

$$T_M = [VO^{2+}] + [VOA] + [VOAL^-] \quad \ldots (1)$$

$$T_{OH} + [H^+] = 2[VOA] + 4[VOAL^-] + [HA^-] + 2[A^{2-}] + [HL] \quad \ldots (2)$$

$$T_A = [H_2A] + [HA] + [A^{2-}] + [VOA] + [VOAL^-] \quad \ldots (3)$$

$$T_L = [H_2L^+] + [HL] + [VOAL^-] \quad \ldots (4)$$

where T_M, T_A and T_L represent the total concentrations of metal, primary and secondary ligand species respectively and T_{OH} is the concentraiion of the base added to the reaction mixture during the titration. The hydrolysis of 1 : 1 VO^{2+}-oxalic acid/phthalic acid/maleic acid chelate VOA were also considered to be negligible in presence of the secondary ligand.

In a 1 : 1 : 1 reaction mixture, using the equations (1)-(4) and relations for the dissociation constants of ligands and equilibrium constant (K_1) of the reaction : $VO^{2+} + H_2A \rightleftharpoons VOA + 2H^+$, it may be shown that :

$$a[VO^{2+}]^2 + b[VO^{2+}] - c = 0 \quad \ldots (5)$$

where, $a = \left(2 + \frac{k_1}{[H^+]}\right)\frac{K_1}{[H^+]^2}$,

$b = 2xy + \left(1 - \frac{k_1 k_2}{[H^+]^2}\right)y + x$,

$c = \{(4-m)\, T_M - [H^+]\}xy$

$x = \left(1 + \frac{k_1}{[H^+]} + \frac{k_1 k_2}{[H^+]^2}\right)$, $\quad y = \left(1 + \frac{k'_1}{[H^+]}\right)$

k_1 and k_2 are the dissociation constant of the dicarboxylic acid and k'_1 the first dissociation constant of pyridine-2-aldoxime. The equilibrium concentration of the free vanadyl ions present in the reaction mixture at various points of titration curves for ternary systems was obtained by solving equation (5). The concentrations of other species involved in the equilibrium relations was then calculated from the above equations and also the values of equilibrium constants K′ and K″ of the reactions (i) and (ii) respectively.

Stability constants of 1 : 1 : 1 mixed-ligand chelates : The stability constant of the ternary com-

plex which may be defined as

$$K_{MAL} = \frac{[VOAL^-]}{[VOA][L^-]}$$

was determined by the expression :

$$K_{MAL} = \frac{K'}{k'_1 k'_2} \qquad \ldots \quad (6)$$

where k'_1 and k'_2 are the dissociation constants of the secondary ligand.

The overall stability constant of the mixed-ligand chelate

$$\beta_{MAL} = \frac{[VOAL^-]}{[VO^{2+}][A^{2-}][L^-]}$$

was calculated by the expression

$$\beta_{MAL} = \frac{K''}{k_1 k_2 k'_1 k'_2} \qquad \ldots \quad (7)$$

Constant values of the equilibrium and stability constants have been obtained at all points of titration curves before the precipitation occurs at about m=3.2, 2.4 and 2.2 in the systems VO^{2+}-oxalic acid/phthalic acid/maleic acid—pyridine-2-aldoxime respectively. The values are presented in Table 2.

TABLE 2—EQUILIBRIUM AND CHELATE FORMATION CONSTANTS OF MIXED-LIGAND CHELATES

Systems	$-\log K'$	$-\log K''$	$\log K_{MAL}$	$\log \beta$
VO^{2+}-Oxalic acid-pyridine-2-aldoxime	5.89±0.18	6.30±0.13	8.18±0.18	12.83±0.13
VO^{2+}-Phthalic acid-pyridine-2-aldoxime	4.95±0.03	8.87±0.03	8.62±0.03	12.68±0.03
VO^{2+}-Maleic acid-pyridine-2-aldoxime	4.38±0.12	8.12±0.12	9.24±0.12	13.65±0.12

Although the formation of hydroxo derivatives of 1 : 1 : 1 mixed-ligand complexes have been inferred on the basis of the titration curves, the values of the formation constants for these complexes could not be calculated due to the appearance of a solid phase at an early stage.

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...bility Constants of Binary Complexes of Lanthanons with Thiotropolone

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Stability constants of complexes of La(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III), Yb(III) and Y(III) with thiotropolone have been determined potentiometrically, in 50% (v/v) aqueous dioxan medium at various ionic strengths of sodium perchlorate. The method of Bjerrum and Calvin, as modified by Irving and Rossotti, has been used to find out the values of $\bar{n}$ and pL. The stability constants have been calculated on IBM 360 computer using Weighted Least Squares Method. The values of S_{min} have also been calculated. The order of stability constants was found to be :

La<Pr<Nd>Sm>Gd>Y>Dy>Yb

THE lanthanons are remarkable for their similarity in chemical properties, which is due to the nearly identical configurations of the electrons available for bond formation. Moeller[1] has reviewed the work on complexes of lanthanons. Complexing ability of thiocarboxylic acids has also been studied potentiometrically[2]. In the present communication, we are reporting the values of stability constants of some trivalent lanthanon ion complexes with thiotropolone at various ionic strengths of sodium perchlorate.

Experimental

Apparatus and Reagents—A Beckman pH-meter, SS-2 model, in conjunction with a glass (0-14 pH range) and calomel electrode assembly was used for pH measurements. All metal ion solutions were prepared from A.R. lanthanon nitrate samples, obtained from Indian Rare Earth Ltd. and their solutions were standardised by gravimetric methods and complexometrically, using xylenol orange as indicator. Thiotropone was prepared by the method of Nozoe et al[3,4] and its solution was prepared by dissolving requisite amounts in dioxan.

The solution of known strength of tetramethyl ammonium hydroxide (TMAH) (E. Merck, A.G. Darmstadt) was prepared in 50 : 50 (v/v) dioxan-water mixture.

The titrations were carried out in a closed cell in an atmosphere of nitrogen which was presaturated with the solvent before it entered the reaction solution. Dioxan (AnalaR, B.D.H.) was purified by refluxing with sodium wire for 24 hours and was freshly distilled over sodium before use. Sodium perchlorate (Riedel) was added to all the solutions to keep the ionic strength constant. Potassium hydrogen phthalate buffers were used to standardise the pH-meter. All other reagents used were of reagent grade. All measurements were carried out at $30 \pm 1°$.

The following solutions (total volume 19.7 ml due to the contraction in volume from 20 ml to 19.7 ml) were titrated against N/25 tetramethyl ammonium hydroxide in 50% aqueous dioxan (v/v) for determining the stability constants of thiotropolone complexes at various ionic strengths :

Ist set

(i) 3.0 ml $HClO_4$ (0.02 M)+2.0 ml $NaClO_4$ (2.0 M)+0.5 ml KNO_3 (0.02 M)+4.5 ml H_2O+10 ml dioxan.

(ii) 3.0 ml $HClO_4$ (0.02 M)+2.0 ml $NaClO_4$ (2.0 M)+0.5 ml KNO_3 (0.02 M)+4.5 ml H_2O+10.0 ml ligand (0.01 M) in dioxan.

(iii) 3.0 ml $HClO_4$ (0.02 M)+2.0 ml $NaClO_4$ (2.0 M)+0.5 ml metal nitrate (0.02 M)+4.5 ml H_2O+10.0 ml ligand (0.01 M) in dioxan.

In sets II and III the requisite amounts of $NaClO_4$ were added to maintain the ionic concentration at 0.2 M $NaClO_4$ to 0.005 M $NaClO_4$ respectively.

In all cases, corrections for changes in volume on mixing, dioxan and aqueous solutions, as well as changes in volume which take place during the titrations, have been made.

The pH-meter readings were plotted against the volume of N/25 TMAH added. The additional amount of TMAH needed to reach the same pH in the presence of metal ions is due to the liberation of hydrogen ions by complex formation between the ligand and the metal ions.

From the above titrations curves, the values of $\bar{n}$ and pL have been calculated using Irving and Rossotti method[5]. The corresponding values of stability constants have been calculated using Weighted Least Squares Method of Sullivan et al[6].

This program assigns a weight W_i to each residual U_i and uses matrix algebra to solve the set of equations

$$\frac{\partial S}{\partial \beta_n} = 0$$

where $S = \sum_i W_i U_i$ and β_n is the nth overall formation constant.

β_n values were again calculated by attaching to them appropriate weight factors computed from first set of β_n and the cycle is repeated till a change of less than one part per thousand was obtained in each β_n. This determines that set of β_n which makes the function $U = \left[\sum_{n=0}^{N} (y-x-nz)\ \beta_n \chi^n\right.$ nearest to zero by minimizing $S = \sum_{i=1}^{I} W_i U^2\ (x_i y_i z_i)$, with respect to variation in β_n. S_{min} values have been calculated which have the same significance as χ^2, with k degrees of freedom[7]. Stability constants have also been calculated by Bjerrum's half integral method and the results obtained by the two methods are summarized in Tables 1-4. The complexes of lanthanons with donors other than nitrogen and oxygen have been very little studied. In thiotropolone, the chelating sites are oxygen and sulphur. The values of log K_n reflect the following trends :

(i) Log K_1 values rise regularly from lanthanum to neodymium. Subsequently, value of log K_1 decreases right up to ytterbium. The order of log K_1 values has been found to be :

$$La < Pr < Nd > Sm > Gd > Y > Dy > Yb$$

The similar trends have been observed in the case of α-mercaptopropionic acid and β-mercaptopropionic acid[8,9]. The results indicate that either sulphur atom is a poor donor for lanthanon ions or some steric hindrance due to bigger size of sulphur atom hinders the formation of complexes.

(ii) Log K_2 and log K_3 values increase regularly from lanthanum to neodymium complexes, but from samarium to ytterbium complexes, they become nearly same or decrease. This also may be probably result of steric hindrance to the attachment of the second molecule of the ligand to the 1 : 1 complex[9], which becomes more significant in the case of heavier lanthanon ions only because of the slight variations in the ionic radii of lanthanons which are close neighbours.

(iii) Log K_1 values for yttrium complexes are found to be quite close to the values of gadolinium complexes. Depending upon the nature of the

TABLE 1—STABILITY CONSTANTS OF COMPLEXES OF LANTHANONS WITH THIOTROPOLONE AT VARIOUS IONIC STRENGTHS CALCULATED BY BJERRUM'S HALF INTEGRAL METHOD

Metal ion	μ=0.2 M $NaClO_4$			μ=0.1 M $NaClO_4$			μ=0.005 M $NaClO_4$		
	log β_1	log β_2	log β_3	log β_1	log β_2	log β_3	log β_1	log β_2	log β_3
H^+	7.02	–	–	7.12	–	–	7.47	–	–
La (III)	5.02	9.20	–	5.27	9.64	–	5.40	9.78	–
Pr (III)	5.37	9.91	–	5.45	9.87	–	5.80	10.55	–
Nd (III)	5.70	10.54	14.14	6.10	11.22	15.53	6.45	11.92	16.17
Sm (III)	5.56	10.23	14.11	6.00	10.86	14.84	6.08	11.23	15.28
Gd (III)	5.45	10.06	13.56	5.70	10.29	13.97	5.90	10.80	14.62
Dy (III)	5.20	9.60	12.84	5.42	9.86	13.43	5.55	10.20	13.96
Yb (III)	4.95	8.82	–	5.17	9.36	–	5.35	9.65	–
Y(III)	5.35	9.87	13.13	5.55	10.03	13.68	5.85	10.65	14.45

TABLE 2—STABILITY CONSTANTS AND S_{min} VALUES OF LANTHANON COMPLEXES WITH THIOTROPOLONE CALCULATED BY WEIGHTED LEAST SQUARES METHOD
(μ=0.2 M $NaClO_4$)

Metal ion	log K_1	log K_2	log β_2	log K_3	log β_3	S_{min}
La (III)	4.67	4.15	8.82	–	–	0.3822
Pr (III)	4.84	4.32	9.16	–	–	0.0249
Nd(III)	5.31	4.50	9.81	3.33	13.14	0.0134
Sm (III)	5.22	4.46	9.68	3.27	12.95	0.0782
Gd (III)	4.99	4.41	9.40	3.25	12.65	0.0042
Dy (III)	4.81	4.45	9.26	3.02	12.28	0.0386
Yb(III)	4.65	3.90	8.55	–	–	0.1134
Y(III)	4.94	4.40	9.34	3.25	12.59	0.0174

TABLE 3—STABILITY CONSTANTS AND S_{min} VALUES OF LANTHANON COMPLEXES WITH THIOTROPOLONE CALCULATED BY WEIGHTED LEAST SQUARES METHOD
(μ=0.1 M $NaClO_4$)

Metal ion	log K_1	log K_2	log β_2	log K_3	log β_3	S_{min}
La (III)	4.75	4.35	9.10	–	–	0.0052
Pr (III)	4.92	4.63	9.55	–	–	0.0054
Nd (III)	5.38	4.87	10.25	4.19	14.44	0.0276
Sm(III)	5.31	4.70	10.01	3.91	13.92	0.0083
Gd(III)	5.11	4.67	9.78	3.58	13.36	0.7515
Dy(III)	4.82	4.66	9.48	3.19	12.67	0.0077
Yb (III)	4.69	4.04	8.73	–	–	0.0098
Y(III)	5.08	4.62	9.70	3.37	13.07	0.0777

TABLE 4—STABILITY CONSTANTS AND S_{min} VALUES OF LANTHANON COMPLEXES WITH THIOTROPOLONE CALCULATED BY WEIGHTED LEAST SQUARES METHOD

(μ = 0.005 *M* $NaClO_4$)

Metal ion	log K_1	log K_2	log β_2	log K_3	log β_3	S_{min}
La (III)	5.25	4.47	9.72	–	–	0.0037
Pr (III)	5.62	4.78	10.40	3.78	14.18	0.0170
Nd (III)	5.90	5.81	11.70	4.29	15.99	0.0780
Sm (III)	5.86	4.83	10.69	3.48	14.17	0.0103
Gd (III)	5.74	4.84	10.58	3.67	14.25	0.0867
Dy (III)	5.44	4.79	10.13	3.66	13.79	0.0032
Yb (III)	5.12	4.45	9.57	–	–	0.0103
Y (III)	5.70	4.80	10.50	3.66	14.16	0.0175

ligand, the stability constant values of yttrium complexes are at times close to those of dysprosium complexes and at others close to praseodymium. Because of its size, yttrium should be found near holmium except when lack of ligand field stabilization moves it closer to gadolinium. Possibly, polarizability effects or/and minor but variable contributions of covalent bonding are responsible for the erratic behaviour of yttrium[10].

(iv) A study of dependance of stability constants on ionic strengths shows that there is a regular and slow decrease in the values of stability constants with increase in ionic strength, which is in agreement with the trend in variation of pK_a values of the ligand.

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Study of Equilibrium Constants of UO_2^{2+}-Malonic Acid Complexes at Various Ionic Strengths and in Dioxane-Water Mixtures

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The equilibrium constants of UO_2^{2+}-malonic acid system in 20, 40, 60 and 80% (v/v) dioxane-water mixtures have been investigated by pH metric method at 0.032, 0.052, 0.072, 0.092 and 0.112 ionic strengths. It is observed that UO_2^{2+} forms 1 : 1 and 1 : 2 complexes with malonic acid in all solvent mixtures.

The distance of closest approach 'a' between the uranyl ion and malonic acid calculated for 1 : 1 complex in aqueous and 20% (v/v) dioxane-water mixture was found to be 4A°. The complexation equilibria for the formation of 1 : 1 and 1 : 2 chelates :

(i) (a) $UO_2^{2+} + H_2L \rightleftharpoons UO_2HL^+ + H^+$

(b) $UO_2^{2+} + HL^- \rightleftharpoons UO_2L + H^+$

(ii) $UO_2^{2+} + 2HL^- \rightleftharpoons UO_2L_2^{2-} + 2H^+$

are proposed. pK/log K values increase with increase in dioxane percentage.

THE stability of transition metal complexes with a great variety of ligands have been studied[1]. Uranyl complexes of dicarboxylic acids have been reported in the literature[2-6]. Rajan and Martell[7,8] have thoroughly looked into the interactions of uranyl ion with organic ligands and correlated the stability constants of their chelates with the acid dissociation constants of the ligand acids. It is observed that uranyl ion forms 1 : 1 as well as 1 : 2 chelates with malonic acid in aqueous medium[9]. As a part of our studies[10,11] on metal complexes with dicarboxylic acids, now we report uranyl complexes with malonic acid in dioxane-water mixtures. The present work was undertaken to examine (i) whether malonic acid can form 1 : 2 chelate in solvent mixtures with dielectric constants lower than water, (ii) the exact complexation equilibria of the complexes, (iii) inter ionic distance between the ligand and metal ion and (iv) the effect of dielectric constant on the stabilities.

Experimental

The chemicals used were Fluka products. Malonic acid obtained from Fluka (Germany) was purified by repeated crystallization. The concentration of uranyl ion was estimated by the standard procedure[12]. All solutions were prepared in glass distilled water. The details regarding other chemicals, measurements of pH are given in an earlier paper[13,14].

The ionic strength of the solution was maintained by the addition of appropriate amounts of 1M sodium perchlorate solution. The calibration of glass electrode in different solvent mixtures and conversion of B value (pH meter reading) into hydrogen ion concentration was done by the method of Van Uitert et al[15,16].

Results and Discussion

The proton-ligand and metal-ligand stability constants were calculated by the method of Irving anh Rossotti[17,18]. The accurate values of pK were calculated by pointwise calculations and are set out in Table 1, Initially log K_1 and log K_2 values were obtained by pointwise calculations since the difference (log K_2 - log K_1) was less than 2, their accurate values were calculated by the method of least-squares (Table 2). The maximum value of $\bar{n}$

TABLE 1—pK VALUES OF MALONIC ACID IN DIOXANE-WATER MIXTURES AT VARIOUS IONIC STRENGTHS

Temp. = 30°

μ	pK_1/pK_2	Dioxane percentage (v/v)				
		0*	20	40	60	80
0.032	pK_1	5.59	6.37	7.38	8.28	10.07
	pK_2	2.83	3.29	3.93	4.85	7.05
0.052	pK_1	5.50	6.25	7.22	8.21	10.04
	pK_2	2.80	3.23	3.88	4.82	6.98
0.072	pK_1	5.47	6.22	7.19	8.16	9.99
	pK_2	2.73	3.18	3.85	4.80	6.96
0.092	pK_1	5.40	6.12	6.97	8.10	9.90
	pK_2	2.70	3.14	3.80	4.77	6.76
0.112	pK_1	5.30	6.08	6.79	8.05	9.87
	pK_2	2.68	3.10	3.74	4.74	6.69

* Values from Ref. 9

* For correspondence.

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TABLE 2—log K VALUES OF UO_2^{2+}-MALONIC ACID COMPLEXES IN DIOXANE-WATER MIXTURE AT VARIOUS IONIC STRENGTHS

Temp. = 30°

μ	log K_1/log K_2	Dioxane percentage (v/v) 0*	20	40	60	80
0.032	log K_1	5.87	6.42	8.61	11.11	14.72
	log K_2	3.54	3.88	5.07	6.65	11.08
0.052	log K_1	5.75	6.25	8.12	9.98	14.62
	log K_2	3.66	4.07	5.18	6.80	11.12
0.072	log K_1	5.71	6.12	7.82	9.69	14.46
	log K_2	3.70	4.18	5.38	6.91	11.17
0.092	log K_1	5.62	6.04	7.62	8.90	14.20
	log K_2	3.76	4.36	5.40	6.96	11.20
0.112	log K_1	5.56	5.93	7.41	8.35	14.16
	log K_2	3.80	4.43	5.50	7.07	11.24

* Values from ref. 9

at each ionic strength was around 1.9, The formation of 1 : 2 complex was proved by the standard procedure[19]. The standard deviation of these values was between 0.01 and 0.05. A representative data, i.e., UO_2^{2+}-malonic acid in 80% (v/v) dioxane-water mixture explain adequately the precision of the experimental work (Table 3).

TABLE 3—CALCULATIONS OF STABILITY CONSTANTS OF UO_2^{2+}-MALONIC ACID. MEDIUM . 80% (v/v) DIOXANE-WATER

Temp. 30 ± 0.1° $\mu = 0.11\ M$ ($NaClO_4$)

B	$\bar{n}_{expt.}$	$\bar{n}_{calcd.}$	pL	$\Delta\bar{n}$
2.0	0.372	0.370	15.064	0.002
2.2	0.503	0.525	14.681	−0.022
2.4	0.619	0.629	14.288	−0.010
2.6	0.662	0.655	13.896	0.007
3.6	1.343	1.338	11.939	0.005
3.8	1.486	1.482	11.551	0.004
4.0	1.568	1.540	11.168	0.028
4.2	1.698	1.690	10.771	0.008
4.4	1.753	1.742	10.376	0.011

Slope = 2.537×10^{25} log K_{ML_1} = 14.176

Intercept = 1.502×10^{14} log K_{ML_2} = 11.230

Standard deviation : 0.014

It was observed that at each percentage of dioxane, the values of pK_1, pK_2 and log K_1 decrease and log K_2 increase with the increase in ionic strength. The magnitude of the increment is, however, not the same for all dioxane-water mixtures. It is higher at the higher percentage of dioxane. The Bronsted equation[20]

$$\log K = \log K^\circ + A\Delta z^2$$

and

$$pK = pK^\circ - A\Delta z^2$$

were used to determine the magnitude of Δz^2 in dioxane-water mixtures, where,

$$\Delta z^2 = z^2_{product} - z^2_{reactants}$$

The values of A and B at various percentages of dioxane-water mixtures[30] were taken from the work of Harned and [illegible].

The plots of pK/log K against $\sqrt{\mu}$

A linear relationship between pK and log K against $\sqrt{\mu}$ was obtained for all percentages of dioxane-water mixtures for all the systems. The values of Δz^2 obtained from the slopes of these straight lines are given in Table 4.

TABLE 4—VALUES OF Δz^2 OBTAINED FROM THE SLOPES

Reaction constant	Dioxane percentage (v/v) 0	20	40	60	Expected values on the basis of complex equilibria
pK_1	2.24	1.72	1.09	0.24	2
pK_2	3.37	2.70	2.94	0.61	4
log K_1	3.87	4.52	7.94	7.00	−4
log K_2	3.10	3.04	1.71	0.24	4

The observed Δz^2 are less than the expected values. The discrepancy between the two is significant at higher percentage of dioxane. An identical observation was recorded by Jahagirdar and Khanolkar for Cu^{2+}-3, 5-dibromosalicylic acid[22].

The pK/log K against $\sqrt{\mu}/1+\sqrt{\mu}$ and $\sqrt{\mu}/1+\sqrt{\mu}-0.3\mu$ also gave linear plots without any improvement in the magnitude in Δz^2. The observed values thus are away from the expected ones. The discrepancy may be due to the fact that the value for 'a' was fixed at 3.3A°. It was, therefore, decided to calculate 'a' values in order to understand the discrepancy.

Calculation of accurate 'a' value

The most accurate value of 'a' can be calculated by method of successive approximations by putting different values of 'a' in the Bronsted and Christiansen[23] equation :

$$\log K = \log K^\circ + \frac{A\Delta z^2 \sqrt{\mu}}{1 + B.a\sqrt{\mu}}$$

and observing its influence on the log K° against $\sqrt{\mu}$ plots. It is expected that for the correct value of 'a', log K° against $\sqrt{\mu}$ plot should be linear and parallel to the $\sqrt{\mu}$ axis. The calculations were made by taking the values of A and B as 0.5161 and 0.330×10^8 respectively in water at 30°[24]. None of the plots (except for a = 4A°) is parallel to the $\sqrt{\mu}$ axis. It may, therefore, be concluded that the value of 'a' for UO_2^{2+}-malonic acid in aqueous medium is 4A°. This was further confirmed from the plots of log K against $\sqrt{\mu}/1+B.a\sqrt{\mu} = \sqrt{\mu}/1+1.3204\sqrt{\mu}$ which gave the slope value −4.24 identical to the one expected for 1 : 1 complex for UO_2^{2+}-malonate in 20% dioxane-water mixtures. It is observed that the values of 'a' remain constant in both the cases, i.e., 4A°.

The closest distance of approach between the metal ion and the ligand is given by the expression $a = r_1 + r_2 - \Delta$, where r_1 and r_2 are the radii of a

cation and anion and Δ is penetration distance. The total size of the ligand molecule is roughly estimated from the knowledge of bond length and bond angles. In aqueous solution uranyl ion is present as hydrated ion and the total size of the ion was calculated by considering a unimolecular layer in the inner hydration sphere. The total size of hydrated uranyl ion being thus 3.93A°, the magnitude of Δ would be 1.5A°. This value arises because when anion and cation meet the anion penetrates in the hydration sheath of the cation by this distance. This penetration arises because of the attraction of a negatively charged ligand for a positively charged metal ion.

The nature of complexation equilibria

The interaction of uranyl ion with both the species, i.e., undissociated malonic acid (H_2L) and dissociated species ($H\bar{L}$) is possible as pK_1 value of malonic acid is 2.68[9]. The formation of 1 : 1 and 1 : 2 chelates occur by the equilibria :

$$\text{(i) (a)}\quad UO_2^{2+}+H_2L \rightleftharpoons UO_2HL^{+}+H^{+}$$

$$\text{(b)}\quad UO_2^{2+}+H\bar{L} \rightleftharpoons UO_2L+H^{+}$$

$$\text{(ii)}\quad UO_2^{2+}+2H\bar{L} \rightleftharpoons UO_2L_2^{2-}+2H^{+}.$$

The magnitude of Δz^2 for the reactions (a) and (b) are -2 and -4 respectively. The calculated value from ionic parameters is -4.24 close to -4. It is, therefore, concluded that the complexation is occurring by the equilibrium (b). In addition to this, in dioxane-water mixture the B values (*p*H meter readings) are around 3.0 at $\bar{n}=0.5$ for 20, 40, 60 and 80% (v/v) dioxane-water mixtures, the practical pK_1 values are 2.95, 3.40, 3.87 and 4.15 respectively. At B = 3.0, the concentration of H_2L would therefore be greater than $H\bar{L}$ at higher percentage of dioxane. Finally at 80% of dioxane $[H_2L] \gg [H\bar{L}]$. The complexation reactions 'a' and 'b' proceed at 20, 40, 60 while 'b' is prominent for the observed magnitude of Δz^2, for 1 : 1 chelates.

Effect of dielectric constant on stabilities

In the system studied, the values of *p*K/log K increase with decrease in dielectric constant. The plots of *p*K/log K against 1/D were non-linear while those against mole fraction exhibit linearity. In the plots of *p*K vs 1/D, the first three points invariably fell on a straight line.

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Investigations on Lanthanum(III) and Yttrium(III) Chelates with Mordant Black Dyes

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The chromogenic reactions of lanthanum(III) and yttrium(III) with various mordant black dyes viz. 1-(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulphonate (Eriochrome black T, abbr. Erio T), 1-(1-hydroxy-2-naphthylazo)-2-naphthol-4-sulphonate (Solochrome black 6BN, abbr. Solo 6BN) and 1-(1-hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulphonic acid (calmagite) have been investigated in aqueous media at 25° and ionic strength 0.1 *M* ($NaClO_4$). Composition and useful analytical parameters have been evaluated for the chelates. Stepwise formation constants have been determined potentiometrically using Calvin-Bjerrum *p*H titration technique as used by Irving and Rossotti.

A number of *o,o'*-dihydroxyazo dyes (mordant black dyes) give interesting chromogenic reactions with metal ions. They have been extensively used in the detection, determination of microamounts of the metals and as metallochromic indicators in complexometric titrations. The important dyes of this group are Erio T, Solo 6BN and Calmagite. These ligands have been used as metallochromic indicators in complexometric titrations[1-6] and several metal chelates of these ligands[6-13] have been investigated spectrophotometrically. Recently Mushran and coworkers[14-17] have studied vanadium(IV), uranium(VI), indium(III), gallium(III), aluminium(III), molybdenum(VI) and tungsten(VI) chelates of these ligands spectrophotometrically and potentiometrically.

Experimental

Materials : The metal solutions were prepared by dissolving lanthanum chloride (E. Merck) and yttrium chloride (AR, BDH) in double distilled water and were estimated gravimetrically by precipitating metal oxalates and subsequent ignition and weighing as oxide. The solutions of required strength were then made by suitable dilution. The solutions of Erio T (Riedel, Germany), Calmagite (Fluka, Switzerland) were prepared by dissolving a weighed quantity in double distilled water. Solo 6BN (BDH, England) was dissolved in 10 per cent. ethanol. Sodium hydroxide, sodium perchlorate and perchloric acid solutions were prepared in double distilled water and were standardized by usual methods.

Instruments : A Leeds-Northrup *p*H meter with glass-calomel electrode assembly was used for *p*H measurements. The scale was standardized using L & N buffer supplied with the instrument. Absorbance measurements were made with a Beckman DU spectrophotometer with 10 mm quartz cells.

Spectrophotometric studies

Conditions of Study

Instantaneous colour formation takes place when reagent and metal solutions are mixed at *p*H 8,5 to 9.8. The complexes were investigated at *p*H 8.5±0.1 (boric acid – borax buffer). The colour intensity remains constant even up to 24 hours. Addition of sodium perchlorate has no effect on absorbance. The ionic strength of the mixtures was maintained constant (0.1 *M*) with sodium perchlorate. The measurements were made at 25°.

Several mixtures containing different proportions of metal and reagent solutions were prepared and *p*H and ionic strength were fixed. The total volume of the mixtures was kept 25 ml. The absorption spectra were recorded from 400-600 nm. The Vosburgh and Cooper[18] method (Fig. 1) showed formation of only one complex in each system. The λ_{max} of Erio T, Solo 6BN and Calmagite are at 560, 570 and 570 nm respectively under the conditions of study. The λ_{max} of lanthanum(III) and yttrium(III) chelates with the three reagents are 540, 530 and 520 nm respectively.

Composition of the Chelates

The composition ML_3 was established for the chelates. Similar results were obtained by applying continuous variation[19], mole ratio[20] and straight line[21] (Figs. 2 and 3) methods.

Analytical Applications

For the photometric determination of lanthanum(III) and yttrium(III) using these ligands,

* For correspondence.

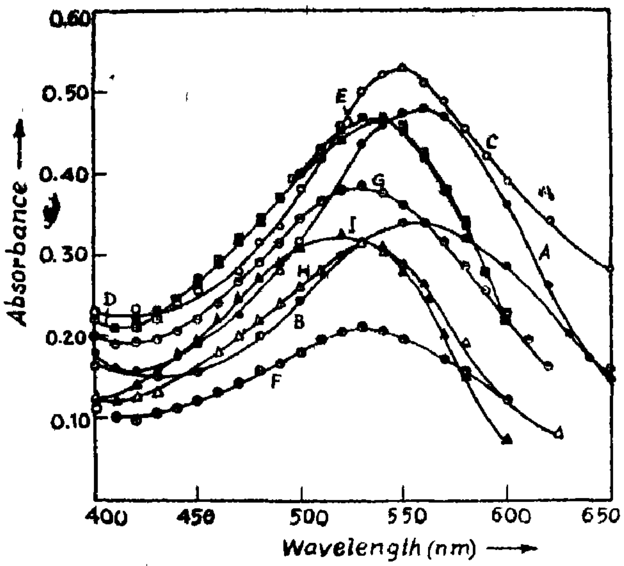


Fig. 1. Absorption spectra at pH 8.5.

A : Erio T ($8 \times 10^{-4} M$), B : La(III)-Erio T chelate ($C_M = 2.66 \times 10^{-4} M$, $C_R = 8 \times 10^{-4} M$), C : Y(III)-Erio T Chelate ($C_M = 2.66 \times 10^{-4} M$, $C_R = 8 \times 10^{-4} M$), D : Solo 6BN ($8 \times 10^{-4} M$) ; E : La(III)-Solo 6BN chelate ($C_M = 2.66 \times 10^{-4} M$; $C_R = 8 \times 10^{-4} M$), F : Y(III)-Solo 6BN chelate ($C_M = 2.66 \times 10^{-4} M$; $C_R = 8 \times 10^{-4} M$) ; G : Calmagite ($8 \times 10^{-4} M$), H : La(III)-Calmagite chelate ($C_M = 2.66 \times 10^{-4} M$, $C_R = 8 \times 10^{-4} M$) ; I : Y(III)-Calmagite chelate ($C_M = 2.66 \times 10^{-4} M$, $C_R = 8 \times 10^{-4} M$).

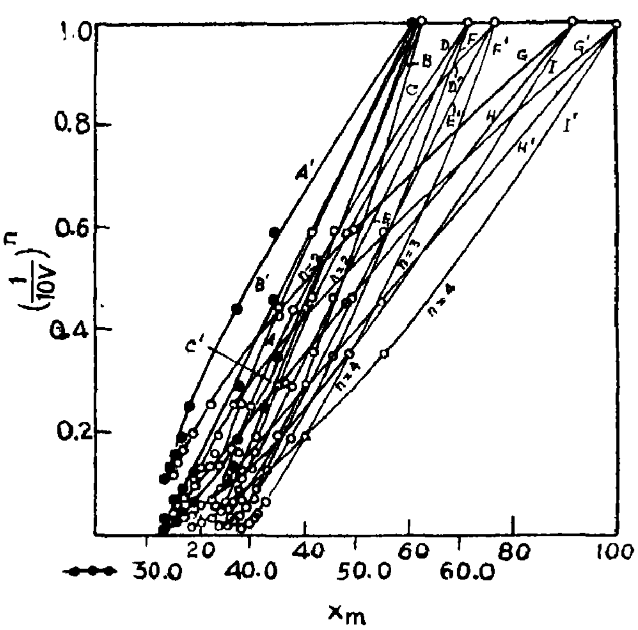


Fig. 2. Straight line plots at 520 nm in the excess of metal ($pH = 8.5$).

$C_M = 4.0 \times 10^{-5} M$; $C_R = 4 \times 10^{-5} M$ (0.1-0.8 ml) A, B, C, La(III)-Erio T : A′, B′, C′, Y(III)-Erio T : D, E, F, La(III)-Solo 6BN ; D′, E′, F′, Y(III)-Solo 6BN ; G, H, I, La(III)-Calmagite ; G′, H′, I′, Y(III)-Calmagite.

important analytical parameters have been evaluated. These are given in Table 1.

TABLE—1 : BEER'S LAW, RINGBOM OPTIMUM RANGES AND SANDELL'S SENSITIVITY

System	Beer's law range (ppm)	Ringbom optimum range (ppm)	Sandell's sensitivity (γ/cm^2)
La(III)-Erio T	0.3-6.7	1.1-6.6	0.007
Y(III)-Erio T	0.2-4.3	1.0-4.2	0.004
La(III)-Solo 6BN	0.3-6.7	1.7-6.6	0.009
Y(III)-Solo 6BN	0.2-4.3	1.4-4.2	0.006
La(III)-Calmagite	0.3-6.7	2.2-6.6	0.005
Y(III)-Calmagite	0.2-4.3	1.4-4.2	0.003

The stability constants of metal-chelates have been computed by the continuous variation method. The values of log K for various systems are given in Table 2.

TABLE—2 : VALUES OF LOG K OF THE CHELATES

System	log K
La(III)-Erio T	13.01
Y(III)-Erio T	13.51
La(III)-Solo 6BN	13.92
Y(III)-Solo 6BN	14.42
La(III)-Calmagite	14.83
Y(III)-Calmagite	15.18

Potentiometric Studies

Bjerrum-Calvin[23,24] pH-titration technique was adopted to investigate the chelates potentiometrically. Protonation constants and formation constants were computed by the method of Irving and Rossotti[25]. The following mixtures were prepared :

(A) 5.0 ml $NaClO_4$ (1.0 M) and 5.0 ml $HClO_4$ (0.119 M).

(B) Mixture A and 25.0 ml Erio T or Solo 6BN or Calmagite (0.001 M).

(C) Mixture B and 5.0 ml $LaCl_3$ or YCl_3 solution (0.0002 M).

Total volume of above mixtures was made 50 ml by adding double distilled water. The mixtures were titrated against 0.3510 M NaOH. From the titration curves so obtained calculations of proton-ligand and metal-ligand stability constants were followed by the method of Irving and Rossotti[25]. The values of $\bar{n}_A$ (average number of protons associated with the ligand), $\bar{n}$ (average number of ligands associated with the metal) and pL (free ligand exponent) were calculated. Protonation constants were evaluated from a plot between $\bar{n}_A$ and pH. The values obtained are given in Table 3.

TABLE—3 : PROTONATION CONSTANTS OF THE LIGANDS $\mu = 0.1M$ ($NaClO_4$), Temp. 25°

Ligand	log K_1^H	log K_2^H	log β^H
Erio T	10.71	7.16	17.87
Solo 6BN	12.45	6.56	19.01
Calmagite	11.98	8.52	20.50

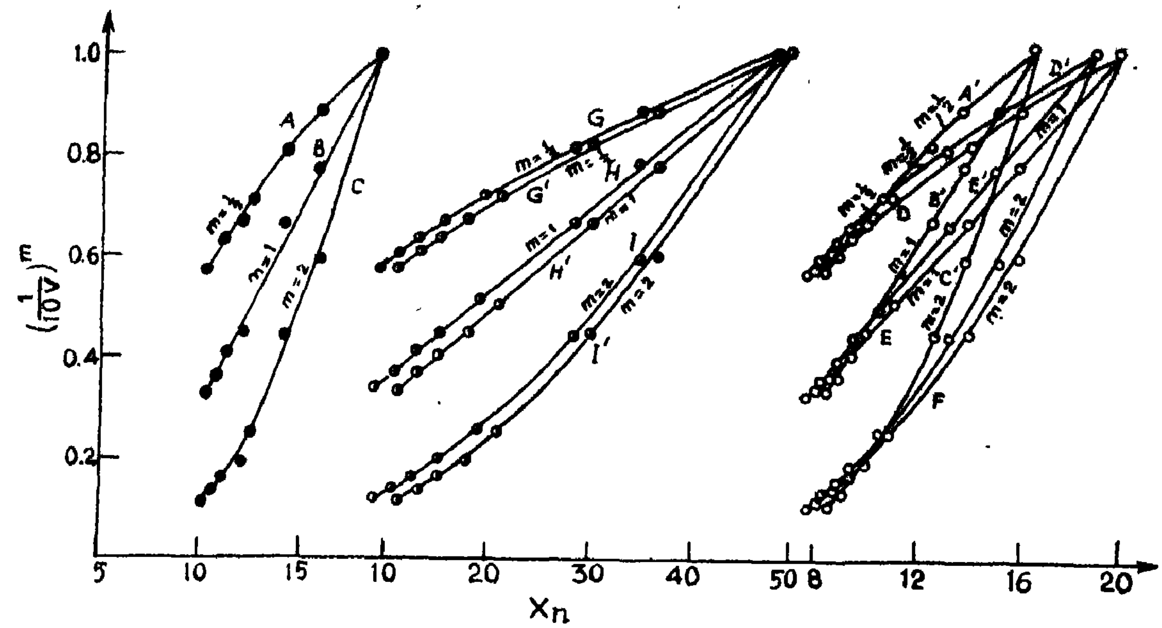


Fig. 3. Straight line plots at 520 nm in the excess of reagent (pH=8.5)
$C_R = 4\times10^{-3}M$; $C_M = 4\times10^{-3}M$ (0.1-0.8 ml) A, B, C, La(III)-Erio T; A', B', C', Y(III)-Erio T; D, E, F, La(III)-Solo 6BN; D', E', F', Y(III)-Solo 6BN, G, H, I, La(III)-Calmagite, G', H', I', Y(III)-Calmagite.

The order of log β^H values, i.e., Calmagite > Solo 6BN > Erio T is of particular interest. The greater protonation constant of Solo 6BN than Erio T is attributed to the absence of $-NO_2$ group in Solo 6BN. Similarly, due to the presence of $-CH_3$ group in calmagite it has relatively greater protonation constant than Solo 6BN.

The stepwise formation constants were evaluated from the formation curves Fig. 4. Results are given in Table 4.

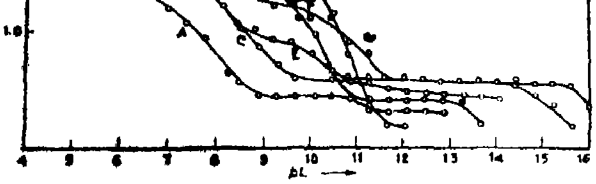


Fig. 4. Formation curves of the chelates.
A = La(III)-Erio T; B = Y(III)-Erio T; C = La(III)-Solo 6BN, D = Y(III)-Solo 6BN; E = La(III)-Calmagite; F = Y(III)-Calmagite.

TABLE—4 : FORMATION CONSTANTS OF THE CHELATES
$\mu = 0.1M$ ($NaClO_4$), Temp. 25°

System	log K_1	log K_2	log K_3	log β
La(III)-Erio T	8.80	5.25	4.30	18.35
Y(III)-Erio T	10.70	9.17	5.35	25.22
La(III)-Solo 6BN	12.20	7.60	5.85	25.65
Y(III)-Solo 6BN	11.15	10.00	6.85	28.00
La(III)-Calmagite	14.60	7.50	6.07	28.17
Y(III)-Calmagite	15.70	7.85	5.90	29.45

It can be seen that log β values lie in the order Y(III)-Calmagite > La(III)-Calmagite > Y(III)-Solo 6BN > La(III)-Solo 6BN > Y(III)-ErioT > La(III)-Erio T. Thus overall formation constants (log β) of above metal chelates follow the same order with respect to ligands as the protonation constants of the ligands. However order of log β for a specific ligand is always Y(III)-chelate > La(III)-chelate.

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Oxalatotitanates

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The preparation of $[Co(NH_3)_6]_2[TiO(C_2O_4)_2]_3.7H_2O$ and oxalatotitanates of protonated organic bases *viz.*, $(BH)_2TiO(C_2O_4)_2$ and $(B'H_2)TiO(C_2O_4)_2$, where B = pyridine, quinoline and guanidine and B' = ethylenediamine and propylenediamine are described. The TGA and DTA data of the compounds indicate the formation of $TiOCO_3$ as an unstable intermediate around 300°. The I.R. data show the compounds to be chelate oxalato complexes.

THE oxalatotitanates[1-7] are of two types, *viz.*, $M^I_2[Ti(C_2O_4)_3]$, where $M^I = (CH_3)_4N$, and $M_2[TiO(C_2O_4)_2]$ where M = Na, K, (pyridine H)$^+$, $\frac{1}{2}$ Ba, etc. The above compounds were studied extensively by others[1-7,17,18]. In the present work the isolation of oxalatotitanates of protonated organic bases, $(BH)_2TiO(C_2O_4)_2$ and $(B'H_2)TiO(C_2O_4)_2$, (where B = pyridine, quinoline and guanidine; B' = ethylenediamine and propylenediamine), are described. The preparation of pyridinium compound reported in this paper was prepared by a method different from that reported by Van de Valde *et al*[7].

From the reaction of potassium oxalatotitanate with hexamminecobalt(III) chloride Marcarovici *et al*[6] isolated the compound $[Co(NH_3)_6]_2[Ti_3O_2Cl_2(C_2O_4)_6].5H_2O$(I). They further reported that this compound on heating at 170° produces $[Co(NH_3)_6]_2[TiO(C_2O_4)_2]_3$(II). But in the present work, the compound(II) was obtained directly from the reaction of potassium oxalatotitanate with $[Co(NH_3)_6]Cl_3$ in aqueous medium, and it was found to correspond to the formula $[Co(NH_3)_6]_2[TiO(C_2O_4)_2]_3.7H_2O$. All the compounds are studied through recording of their I.R. spectra, TGA and DTA data.

Experimental

Hexamminecobalt(III) nitrate, hexamminecobalt(III) chloride and potassium oxalatotitanate were prepared by standard methods[9-11]. Titanium, cobalt and oxalate were estimated by usual standard methods and nitrogen was estimated by semimicro Dumas' method. The analytical data of the compounds are given in Table 1. Hydrated titanium oxide used in the present work was prepared according to Rosenheim and Schutte[2].

Pyridinium oxalatotitanate, $[C_5H_5NH]_2[TiO(C_2O_4)_2].3H_2O$: Hydrated titanium oxide obtained from titanium dioxide was dissolved in a solution of oxalic acid by heating on a water bath. To this solution pyridine was added and the mixture was evaporated on a water bath, cooled and absolute alcohol was added when the compound precipitated out. Filtered, washed with water and with alcohol. The compound was recrystallised from water in the presence of 2-3 drops of pyridine. It was dried to constant weight in air.

The corresponding oxalatotitanates of protonated quinoline, guanidine, propylenediamine and ethylenediamine are obtained in the above manner from calculated amounts of reactants but without the addition of alcohol required for crystallisation. The amines were, however, reacted with calculated amounts of oxalic acid before adding the mixture to hydrated titania dissolved in oxalic acid. The recrystallisation step was also found to be unnecessary.

Hexamminecobalt(III) oxalatotitanate $[Co(NH_3)_6]_2[TiO(C_2O_4)_2]_3.7H_2O$: The compound

TABLE—1

Compounds	Found (%)			Calculated (%)		
	N	Ti	Oxalate	N	Ti	Oxalate
$[PyH]_2[TiO(C_2O_4)_2].3H_2O$	6.25	10.71	39.13	6.17	10.55	38.77
$[QH]_2[TiO(C_2O_4)_2].1.5H_2O$	5.33	9.31	33.39	5.31	9.09	33.40
$[GuH]_2[TiO(C_2O_4)_2].1.5H_2O$	21.78	12.95	45.54	21.71	12.38	46.47
$[EnH_2][TiO(C_2O_4)_2].H_2O$	8.72	14.99	54.05	8.75	14.97	55.01
$[PnH_2][TiO(C_2O_4)_2].0.4H_2O$	8.43	14.85	54.39	8.66	14.82	54.45
$[Co(NH_3)_6]_2[TiO(C_2O_4)_2]_3.7H_2O$	14.10	12.00	43.17	14.38	12.31	45.23

Py = pyridine, Q = quinoline, En = ethylenediamine, Pn = propylenediamine, Gu = guanidine.

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was obtained as a yellow precipitate on adding a solution (40 ml) of hexamminecobalt(III) chloride (1.7 gm) to a solution (75 ml) of potassium oxalatotitanate, $K_2[TiO(C_2O_4)_2].2H_2O$ (3.5 gm). The precipitate was filtered, washed with water anp alcohol, and dried in air. The same product was also obtained on adding a solution of hexamminecobalt(III) nitrate to a solution of hydrated titanium oxide in oxalic acid.

The oxalatotitanates of protonated organic bases are soluble in water but the corresponding hexamminecobalt(III) compound is insoluble in water. All of them are insoluble in common organic solvents. These compounds when dehydrated over P_2O_5 in a vacuum desiccator at room temperature lose water giving anhydrous compounds. The TGA and DTA data were recorded in manually operated instruments by heating the compounds at the rate of 5°/min. The I.R. data were recorded in a Perkin-Elmer apparatus in KBr in the range 400-4000 cm^{-1}.

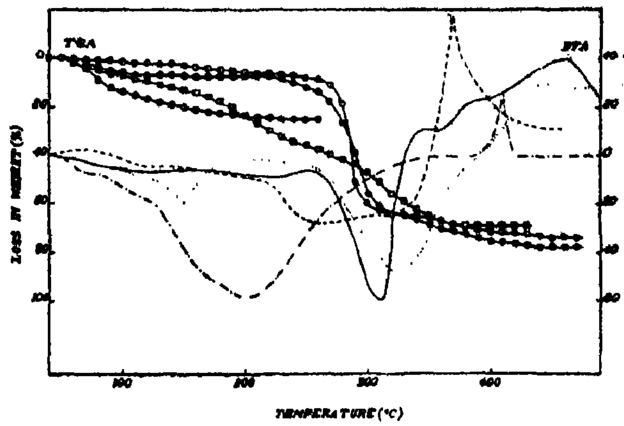


Fig. 2. T.G.A. and D.T.A. data of oxalatotitanates and hydrated titanium dioxide.

$[PnH_2][TiO(C_2O_4)_2]O.H_2O$: —○—○— ; ————

$[GUH]_2[TiO(C_2O_4)_2].1.5.H_2O$: —●—●— ; ....

$[Co(NH_3)_6]_2[TiO(C_2O_4)_2]_3$: —⊡—⊡— ; - - - - - - - -

$TiO_2,1.5H_2O$: —◑—◑— ; —·—·—·—·—·—

Results and Discussion

The oxalatotitanates of protonated organic bases are found to be thermally stable up to 50°. The thermograms of the oxalatotitanates of protonated quinoline, guanidine and ethylenediamine show horizontal stretches in the temperature ranges, 80-110°, 100-200° and 140-170° respectively corresponding to the loss of water of crystallisation. The pyrolysis curves did not show the formation of any stable intermediate compound.

From the TGA and DTA data (Figs. 1 and 2) it may be concluded that probably $TiOCO_3$ is formed

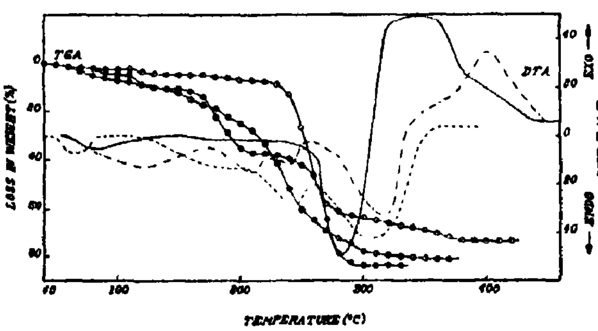


Fig. 1. T.G.A. and D.T.A. of oxalatotitanates.

$[EnH_2][TiO(C_2O_4)_2].H_2O$: —○—○— ; ————

$[PyH]_2[TiO(C_2O_4)_2].3H_2O$: —◑--◑— ; - - - - - - - -

$[QH]_2[TiO(C_2O_4)_2].1.5.H_2O$: —●—●— ; —.—.—.—.—.

as an unstable intermediate (indicated by the endotherms in the DTA curves) in the range 280-330° from the oxalatotitanates of protonated organic bases except in the case of the corresponding quinolinium compound. $TiOCO_3$ then undergoes decomposition to titanium dioxide with the evolution of CO_2 (indicated by exothermic reaction). Another interesting feature noted in the thermal study of the oxalatotitanates of protonated organic bases is that the differential thermograms show broad and ill-defined exotherms probably due to the transformation of amorphous titanium dioxide into crystalline form[7]. The above fact is supported by the DTA of hydrated titanium oxide and titanyl oxalate which show sharp exotherms in the range 400-420°[11] (Fig. 2). The TGA and DTA data of $[Co(NH_3)_6]_2[TiO(C_2O_4)_2]_3$ do not show any remarkable feature. The compound was found to be stable up to 50°. The residue obtained after thermal analysis was found to be the oxides of cobalt and titanium. The exotherm at 370° probably corresponds to the formation of the oxides of cobalt and titanium[8].

The bands for oxalate group in the regions 1720-1750 cm^{-1}, 1380-1430 cm^{-1}, 785-825 cm^{-1} and 520-570 cm^{-1} are attributed to the chelate oxalate complexes[13-15]. The bands for oxalate group observed in the I.R. spectra of the oxalatotitanates of protonated organic bases and of hexamminecobalt(III) ion lie within the regions given above. This suggests that these oxalato complexes are chelate complexes.

The lattice water usually absorb in the regions, 3200-3550 cm^{-1} (antisymmetric and symmetric OH stretching) and at 1600-1630 cm^{-1} (HOH bending)[16]. Similarly, bands of N–H also occur in the regions 3000-3400 cm^{-1}, 1550-1650 cm^{-1} and 1400-1470 cm^{-1}. The oxalatotitanates described here show bands in the regions 2900-3600 cm^{-1}, 1650-1740 cm^{-1}, 1500-1530 cm^{-1} and 1300-1480 cm^{-1} due to H_2O, N–H and C_2O_4 group as indicated above. The band due to HOH bending at 1600-1630 cm^{-1} could not be identified separately due to the superimposition of the band with the O–C–O asymmetric stretching. All the compounds show broad bands in the region 800-900 cm^{-1} which may be due to Ti–O stretchings[12-15].

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Solid State Interaction Between Urea Nitrate and Phosphates of Iron and Aluminium

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Urea nitrate is found to react with the phosphates of iron and aluminium in the solid phase. The interaction occurs on grinding urea nitrate with the tertiary phosphate of iron or aluminium together in a particular ratio for about an hour. The resulting product becomes completely water soluble when the mole ratio of the phosphate to urea nitrate is 1 : 2. The interaction occurs in two steps (i) formation of dibasic phosphate of iron or aluminium in the solid state and (ii) further protonation to soluble monobasic phosphate of iron or aluminium when placed in water in the presence of unreacted urea nitrate.

SOILS having lower *p*H contain higher amounts of aluminium, iron and reductant soluble phosphate. The utilization of phosphorus by plants from these phosphates has been studied by a number of workers[2,3]. Acid soils containing phosphates of iron and aluminium are "unavailable" to plants because these two elements are regarded as the main converters of "available" phosphate to "unavailable" phosphate[1]. To make these phosphates available to plants especially in acid soils is therefore of considerable interest in soil chemistry. In the present investigation the author attempts to find out the solid state interaction between ferric and aluminium phosphates with urea nitrate on the lines earlier reported by the author for rock phosphates[7]. The work consists of grinding a fixed amount of ferric or aluminium phosphate with varying amounts of urea nitrate so as to determine the particular ratio of the phosphate to urea nitrate necessary for rendering it completely water soluble.

Experimental

Since the exact nature of iron and aluminium phosphates in soil is as yet unknown the experiments were carried out with laboratory reagent forms, $FePO_4.2H_2O$ and $AlPO_4.2H_2O$. Urea nitrate was prepared from urea and nitric acid[4]. It was purified by recrystallization. 1 g mole of ferric phosphate or aluminium phosphate was mixed with varying amounts of urea nitrate and ground in an agate mortar for about an hour under dry conditions.

To evaluate the extent of chemical reaction 1 g of the ground mixture was treated with absolute alcohol (in which all the reactants and products except the phosphates are soluble), filtered and in the filtrate the amount of iron nitrate or aluminium nitrate was estimated[5]. To determine the extent of availability of phosphate 1 g of the resultant mixture was leached with 250 ml of water, filtered and the amount of P_2O_5 obtained in the filtrate was taken as water soluble phosphate. The amount of P_2O_5 soluble in 100 ml of 2% citric acid solution in the residue after leaching with water was taken as the citrate soluble phosphate[6].

Results and Discussion

Ferric or aluminium phosphate was mixed with different amounts of urea nitrate and ground in an agate mortar for an hour under dry conditions. The amounts of water and citrate soluble P_2O_5 in such mixtures are presented in Table 1. With increasing urea nitrate content, the percentage of water soluble phosphate increases and finally at the stage of 1 : 2

TABLE 1—WATER AND CITRATE SOLUBLE P_2O_5 IN UREA NITRATE-IRON/ALUMINIUM PHOSPHATE MIXTURES

Compound	Phosphate to urea-nitrate mole ratio	Total P_2O_5 %	Water soluble P_2O_5 %	Citrate soluble P_2O_5 %	Fraction of water soluble P_2O_5 %	Fraction of citrate soluble P_2O_5 %
	1 : 0	42.04	–	–	–	–
	1 : 0.25	38.53	3.37	5.80	8.75	15.06
	1 : 0.50	35.55	6.58	10.76	18.50	30.27
	1 : 0.75	33.02	8.62	13.31	26.10	40.32
$FePO_4.2H_2O$	1 : 1.00	30.82	11.11	18.52	36.04	69.10
	1 : 1.25	28.89	17.72	10.11	61.35	35.00
	1 : 1.50	27.19	20.38	6.54	74.94	24.06
	1 : 1.75	25.68	22.39	3.19	87.25	12.40
	1 : 2.00	24.32	24.30	–	99.90	–
	1 : 0	50.72	–	–	–	–
	1 : 0.25	45.70	3.82	6.83	8.35	14.95
	1 : 0.50	41.58	7.61	12.51	18.05	30.10
	1 : 0.75	38.15	9.87	15.28	25.88	40.06
$AlPO_4.2H_2O$	1 : 1.00	35.23	12.65	21.17	35.92	60.08
	1 : 1.25	32.74	20.06	11.48	61.28	34.92
	1 : 1.50	30.57	22.79	7.28	74.55	23.80
	1 : 1.75	28.67	24.91	3.50	87.10	12.20
	1 : 2.00	26.99	26.89	–	99.62	–

mole ratio cent per cent. water soluble mixtures are obtained. It has been observed that for both elements the mixture on treatment with water first forms a colloidal solution which on keeping for about 15 minutes forms a clear solution.

The conversion of the insoluble phosphates to the soluble form is due to protonation reactions which can take place either when the tertiary phosphate of iron or aluminium and urea nitrate are mixed or when the mixture is placed in water. In the former case ferric nitrate or aluminium nitrate is one of the products which is soluble in absolute alcohol (in which phosphates are insoluble). The nitrate of iron or aluminium formed when a fixed weight of the phosphate is mixed with increasing amount of urea nitrate is estimated and the results are shown in Table 2. The nitrate content in both the cases increases with increasing amount of urea nitrate and reaches a limiting value when the mole ratio of the phosphate to urea nitrate is 1 : 2. Further increase in the urea nitrate content does not give rise to increased amount of the nitrate in the extract. The limiting value of the nitrate found corresponds to one mole of the phosphate mixed with two moles of urea nitrate.

TABLE 2—IRON/ALUMINIUM NITRATE CONTENT IN ETHANOL EXTRACT

(1.87 g $FePO_4.2H_2O$/1.58 $AlPO_4.2H_2O + CO(NH_2)_2.HNO_3$)

Compound	Weight of urea nitrate (g)	Phosphate to urea nitrate mole ratio	$Fe(NO_3)_3/Al(NO_3)_3$ Calculated (g)	Found (g)
	0.31	1 : 0.25	0.16	0.02
	0.62	1 : 0.50	0.32	0.08
	0.93	1 : 0.75	0.48	0.18
	1.23	1 : 1.00	0.65	0.32
$FePO_4.2H_2O$	1.54	1 : 1.25	0.81	0.50
	1.85	1 : 1.50	0.97	0.73
	2.16	1 : 1.75	1.13	0.98
	2.46	1 : 2.00	1.29	1.28
	3.08	1 : 2.50	1.29	1.28
	3.69	1 : 3.00	1.29	1.28
	0.31	1 : 0.25	0.14	0.02
	0.62	1 : 0.50	0.27	0.07
	0.93	1 : 0.75	0.41	0.15
	1.23	1 : 1.00	0.55	0.27
$AlPO_4.2H_2O$	1.54	1 : 1.25	0.69	0.43
	1.85	1 : 1.50	0.83	0.62
	2.16	1 : 1.75	0.97	0.83
	2.46	1 : 2.00	1.10	1.09
	3.08	1 : 2.50	1.10	1.09
	3.69	1 : 3.00	1.10	1.09

Urea nitrate is an ionic salt while phosphates of iron or aluminium are basic and it seems from the above observation that on grinding the mixture an acid-base neutralization reaction occurs on account of an increase in the activation energy of the reaction—

$$3FePO_4 + 3CO(NH_2)_2.HNO_3 = Fe_2(HPO_4)_3 + Fe(NO_3)_3 + 3CO(NH_2)_2 \quad \ldots \text{(i)}$$

$$Fe_2(HPO_4)_3 + 3CO(NH_2)_2.HNO_3 = Fe(H_2PO_4)_3 + Fe(NO_3)_3 + 3CO(NH_2)_2 \quad \ldots \text{(ii)}$$

$$3AlPO_4 + 3CO(NH_2)_2.HNO_3 = Al_2(HPO_4)_3 + Al(NO_3)_3 + 3CO(NH_2)_2 \quad \ldots \text{(i)}$$

$$Al_2(HPO_4)_3 + 3CO(NH_2)_2.HNO_3 = Al(H_2PO_4)_3 + Al(NO_3)_3 + 3CO(NH_2)_2 \quad \ldots \text{(ii)}$$

The protonation reaction occurs in two steps. The first step is a solid-solid reaction whereas the second step is a solid-liquid reaction in which the nitric acid formed by the dissociation of urea nitrate reacts with the dibasic phosphate produced in the first step. This is supported by the fact that the ground mixture on treatment with water first forms a colloidal solution which on keeping for sometimes forms a clear solution.

Probably the reaction between urea nitrate and the tribasic phosphates of iron or aluminium takes place due to the mobility of hydrogen and nitrate ions. At the points of contact of the two solids, protonation of the phosphate occurs as a result of the movement of labile H^+ ions from urea nitrate. The mobility of protons in urea nitrate crystals was established by Kutty and Murthy[5]. This changes the electroneutrality of the tribasic phosphates of iron or aluminium and causes the displacement of Fe^{3+} or Al^{3+} ions which in turn combine with the nitrate present at the interphase resulting in the formation of iron or aluminium nitrate. These steps occurring at the phase boundary are followed by the bulk reaction, the rate of which varies depending upon the particle size of the reactants. The movement of nitrate ions from the bulk takes place due to the concentration gradient set up by the removal of nitrate ions at the surface. On grinding the textural and structural states of solids change and fresh surfaces of the reactants are exposed which enhances the rate of the chemical reaction.

It is well known that by treating an excess amount of tribasic phosphate with a less amount of aqueous acid one cannot produce only dibasic phosphate. A mixture of monobasic phosphate and dibasic phosphate is the eventual product. The experimental results in this investigation show that the protonation by urea nitrate follows a path other than that expected in an aqueous medium. This is supported by the fact that the monobasic phosphate of iron or aluminium is not produced in step (i). Had it been one of the products, the side reaction

$$2Fe(H_2PO_4)_3 + 3CO(NH_2)_2 = Fe_2(HPO_4)_3 + 3CO(NH_2)_2.H_3PO_4$$

$$2Al(H_2PO_4)_3 + 3CO(NH_2)_2 = Al_2(HPO_4)_3 + 3CO(NH_2)_2.H_3PO_4$$

would occur and urea phosphate $CO(NH_2)_2.H_3PO_4$ would have been the resulting product. Urea phosphate is soluble in absolute alcohol. Since no alcohol soluble phosphate is detected in the ground mixture of urea nitrate and tribasic phosphates of iron or aluminium the possibility of formation of monobasic phosphate is ruled out. This further supports the occurrence of step (i). The question

of the participation of water in reaction (i), as adsorbed or otherwise held at the surface is also eliminated by the formation of dibasic phosphate alone. Thus the step (i) is a solid-solid interaction and that the dibasic phosphate formed dissolves in excess of urea nitrate solution in the step (ii) to form monobasic phosphate rendering the whole mixture water soluble.

This investigation indicates that a ground mixture of urea nitrate and tertiary phosphates of iron or aluminium in the mole ratio of 2 : 1 may be used in acid soils as an excellent nitrophosphatic fertilizer. Moreover the insoluble iron and aluminium phosphates of acidic soils may be made available to plants by using urea nitrate.

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Titrimetric Determination of Ti(III) with Vanadium(V) and Vanadium(IV) using Cacotheline and Some Thiazine Dyes as Indicators†

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Titanium(III) can be determined with sodium vanadate or vanadyl sulphate using cacotheline and some thiazine dyes (methylene blue, azure A, azure B, azure C, thionine, new methylene blue and toluidine blue) as indicators in 10-12*M* phosphoric acid medium. This procedure can also be used for the estimation of Vanadium(IV) and Vanadium(V) with standard titanium(III) chloride solution.

TITANIUM(III) was determined with vanadate by direct and indirect[1] titrimetric methods. Similarly titanium(III) was determined with vanadium(IV) by earlier workers[2,3]. So far neutral red, phenosafranine and safranine-T are used as indicators in presence of oxalic acid for the determination of titanium(III) with vanadate[4]. The literature survey reveals that no visual method of estimation of titanium(III) with vanadium(IV) was reported using an indicator. In this paper we present the details of the use of cacotheline and some thiazine dyes (methylene blue, azure A, azure B, azure C, thionine, new methylene blue, and toluidine blue) as indicators for the determination of titanium(III) with sodium vanadate and vanadyl sulphate.

Experimental

Reagents :

Sodium Vanadate Solution : 0.05*N* sodium vanadate solution is prepared and standardised.

Vanadium(IV) Solution : Vanadium(IV) sulphate was prepared by sulphite reduction method and standardised according to the procedure given by Dikshitulu and Gopala Rao[5].

Ti(III) Chloride Solution : 0.1*N* titanium(III) chloride solution was prepared in 2*N* hydrochloric acid and standardised according to the procedure of Breit[6].

0.2% cacotheline and 0.1% aqueous solutions of thiazine dyes are prepared.

Procedure : 40 ml. of syrupy phosphoric acid is taken in the titration vessel. Carbon dioxide is passed through it for 10 minutes. Then an aliquot volume of titanium(III) chloride is run down into the titration vessel. Then the contents are titrated with V(V) or V(IV) solution to the appearance of yellow colour in case of cacotheline (0.5 ml. of solution added near the end-point) or greenish blue colour in the case of thiazine dyes (0.1 ml. of dye solution added from the beginning). Some typical results are presented in Table 1.

TABLE—1. DETERMINATION OF TITANIUM(III) WITH VANADIUM (V) AND VANADIUM(IV) IN 11*M* PHOSPHORIC ACID MEDIUM

Indicator used	Amount of Ti(III) (m. moles × 10^{-1}) Taken (through dichromate method)	Found (through authors' method)
	With Vanadate	
Cacotheline	6.285	6.281
	1.839	1.840
Methylene blue	6.075	6.091
	1.823	1.832
New methylene blue	6.015	6.022
	2.406	2.405
Thionine	5.832	5.839
	2.187	2.198
Toluidine blue	2.406	2.410
	6.015	6.022
Azure A	6.050	6.068
	2.290	2.298
Azure B	5.808	5.816
	3.630	3.641
Azure C	6.015	6.022
	1.208	1.205
	With Vanadium(IV)	
Cacotheline	6.532	6.537
	1.645	1.646
Methylene blue	6.030	6.040
	3.420	3.430
New methylene blue	1.094	1.099
	6.017	6.030
Thionine	6.270	6.271
	3.215	3.216
Azure A	6.156	6.164
	2.730	2.734
Azure B	6.199	6.217
	2.029	2.035
Azure C	6.199	6.217
	1.690	1.698
Toluidine blue	2.188	2.185
	6.017	6.030

† Presented at the Annual Convention of Chemists, 1977 held at Jaipur.

By taking vanadium(V) or vanadium(IV) solutions in the titration vessel and titrating with titanium(III) chloride according to the above procedure, it has been observed that vanadium(V) (0.24 m. moles to 0.60 m. moles) and vanadium(IV) (0.15 m. moles to 0.62 m. moles) can be determined with an average error of 0.3% and 0.35% respectively.

Discussion

An attempt to determine titanium(III) with vanadium(V) or vanadium(IV) in hydrochloric or sulphuric acid medium has been met with failure. In the case of vanadium(V) as an oxidimetric reagent in lower acid concentrations (HCl or H_2SO_4) end-point is not obtained. This is due to the interference of vanadium(III) produced with the indicator reaction. But at higher acidities the interference of vanadium(III) in the indicator reaction is eliminated. Still higher values are obtained for titanium(III). This is due to the low oxidising action of vanadium(IV) (intermediate) on the reduced form of the indicator. Similarly in the case of vanadium(IV) as an oxidant, the end-point cannot be detected either in low or high acid (HCl or H_2SO_4) concentrations.

Gopala Rao and Dikshitulu[7] reported that the formal potential of V(IV)/V(III) couple increases from 0.379-0.702 as phosphoric acid concentration increases from 0.5-12 *M*. From this observation, the authors have found the determination of Ti(III) with feasible vanadium(V) and vanadium(IV) in strong phosphoric acid medium, where the two difficulties experienced in hydrochloric and sulphuric acid media can be easily overcome.

Interferences :

Na^+, K^+, Ba^{2+}, Zn^{2+}, Mg^{2+}, Al^{3+}, Fe^{3+}, Cl^-, $SO_4^=$, acetate, oxalate, borate and tartarate do not interfere.

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A Redox Titrimetric Method for the Determination of Thallium(III)

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Thallium(III) can be quantitatively reduced to thallium(I) using excess of iron(II) at room temperature which requires about half an hour. The time factor can be reduced either by boiling or by using a complexing agent like phosphoric acid. The excess unreacted iron(II) can be titrated either with cerium(IV) sulphate using ferroin as indicator or potassium dichromate using diphenyl amine as indicator.

IRON(II) is one of the versatile reductants known. Arthur John Berry[1] has recommended a procedure for the estimation of thallium(III) in which excess of iron(II) was added to thallium(III) in dilute sulphuric acid medium, heated to boiling, cooled and titrated against standard potassium dichromate using potassium ferricyanide as an external indicator. He has observed that his method gives lower values (about 1.7%) when compared with the values obtained gravimetrically by the iodide method.

The kinetics of the reaction between thallium(III) and iron(II) in sulphuric and perchloric acid media were followed by Johnson Jr[2] and Forchheimer et al[3] respectively.

Johnson (Jr.) preferred to use 6F sulphuric acid medium for the reduction of thallium(III) at room temperature with excess of iron(II) and the subsequent titration of the excess unreacted iron(II) after the reduction is complete, either with cerium(IV) sulphate or with standard potassium dichromate. The redox potential of thallium(III)-thallium(I) system in sulphuric acid medium is sufficiently high (1.2 V) for a satisfactory reductimetric titration of thallium(III) with iron(II) to be carried out. But details of the procedure to be adopted for the estimation and the error involved in the method are not available in these references. In view of the results obtained by determining the formal redox potentials of thallium(III)-thallium(I) system in various acids[4] the details of the reductimetric method for the determination thallium(III) with iron(II) are now worked out by the present authors.

Direct titration of thallium(III) with iron(II) was reported[5] from the same school. As this method needs very high concentration of phosphoric acid (more than 11*M*) a much cheeper method though indirect is developed now.

Experimental

Reagents : Thallium(I) and thallium(III) solutions are prepared from thallous carbonate (B.D.H. sample) and standardized as described earlier[6]. Other reagents used are of analytical reagent grade.

To obtain satisfactory results in the estimation of thallium(III) by indirect method the following conditions must be satisfied.

(1) Thallium(I) formed in the reaction should not interfere in the subsequent titration of the excess of iron(II) with the standard oxidant.

(2) The reaction between thallium(III) and iron(II) should be sufficiently rapid.

(3) The reaction must be stoichiometrically completed even with a little excess of the reductant.

Effect of Thallium(I)

The interference of thallium(I) in the titration of iron(II) with cerium(IV) sulphate is studied by adding increasing quantities of thallium(I) to iron(II) solutions in 0.5*M* sulphuric acid medium and titrating with cerium(IV) sulphate. Typical results obtained by the authors are shown in Table 1.

TABLE 1—EFFECT OF THALLIUM(I) IN THE TITRATION OF IRON(II) WITH CERIUM(IV) SULPHATE IN .5*M* SULPHURIC ACID MEDIUM

Iron(II) taken millimole	Thallium(I) added millimole	Iron(II) found millimole	Percentage error
0.50	0	0.5000	nil
0.50	0.05	0.4996	−0.08
0.50	0.10	0.4998	−0.04
0.50	0.20	0.5002	+0.04
0.50	0.30	0.5000	nil
0.50	0.50	0.5004	+0.08

The results in Table 1 show that thallium(I) does not interfere in the titration of iron(II) in 0.5*M* sulphuric acid medium. However, thallium(I) is found to interfere in the titration if the titration is carried out in hydrochloric acid medium. Also the reduction of thallium(III) by iron(II) is affected in the presence of hydrochloric acid. These facts could be easily understood, if one considers the effect of chloride ion on the formal redox potentials of the thallium system[4]. Hence chloride ion is to be avoided for these determinations.

Rapidity and Stoichiometry of the Reaction

The second and third requirements are checked by following the absorption due to ferric iron (followed spectrophotometrically), one of the products of the reaction. The results of such experiments have shown that the reaction is not sufficiently fast in a medium of 0.5*M* sulphuric acid. Hence the excess iron(II) is titrated, with cerium(IV) sulphate using ferroin as indicator, at various intervals of time and the results obtained are shown in Table 2.

TABLE 2—EFFECT OF TIME ON THE REACTION BETWEEN THALLIUM(III) AND IRON(II)

Time in minutes	Thallium(III) taken millimole	Iron(II) added millimole	Excess of Iron(II) millimole	Thallium(III) computed millimole	% error
0	0.20	0.50	0.4920	0.0040	−98
2	0.20	0.50	0.4800	0.0100	−95
5	0.20	0.50	0.4200	0.0400	−80
10	0.20	0.50	0.3160	0.0920	−54
15	0.20	0.50	0.1400	0.1800	−10
20	0.20	0.50	0.1040	0.1980	− 1.0
25	0.20	0.50	0.1016	0.1992	− 0.4
30	0.20	0.50	0.1000	0.2000	nil
45	0.20	0.50	0.1008	0.1996	− 0.2
60	0.20	0.50	0.0992	0.2004	+ 0.2

The results in Table 2 show that the reaction is complete only in about 30 minutes at room temperature in 0.5*M* sulphuric acid medium when double the amount of iron(II), required for the stoichiometric reduction of thallium(III) is present. It is also clear from the table that iron(II) need not be added too much in excess. Double the quantity required by the stoichiometry of the reaction is enough. Hence titrimetric determination of thallium(III) is attempted.

Indirect Determination of Thallium(III) after Reduction with Iron(II) at Room Temperature

Ten ml of 0.05*M* iron(II) sulphate in 0.5*M* sulphuric acid is added to an aliquot of thallium(III) in 0.5*M* sulphuric acid to which about 30 ml of 0.5*M* sulphuric acid is added and allowed to stand for about half an hour. Then the excess iron(II) is back titrated with standard cerium(IV) sulphate solution using ferroin as indicator. Thallium(III) is calculated from the amount of unreacted excess iron(II). Typical results of such determination are recorded in Table 3.

TABLE 3—INDIRECT DETERMINATION OF THALLIUM(III) AFTER REDUCTION WITH IRON(II) AT ROOM TEMPERATURE

Thallium(III) taken millimole	Iron(II) added millimole	Excess of Iron(II) millimole	Thallium(III) computed millimole	% error
0.0480	0.5000	0.4044	0.0478	−0.4
0.0960	0.5000	0.3080	0.0960	nil
0.1440	0.5000	0.2116	0.1442	+0.15
0.1920	0.7000	0.3164	0.1918	−0.1
0.2400	0.7000	0.2188	0.2406	+0.25

The results in Table 3 show that thallium(III) can be determined indirectly by titration with either cerium(IV) sulphate or potassium dichromate by reducing thallium(III) with excess of iron(II). But the procedure requires lot of time (about 30 minutes) for the completion of the reaction. Hence it is attempted to reduce the time factor.

Indirect Determination of Thallium(III) after Reduction with Iron(II) at Boiling Temperature

Ten ml of 0.05*M* iron(II) in 0.5*M* sulphuric acid is added to an aliquot of thallium(III) in 0.5*M* sulphuric acid medium to which about 30 ml of 0.5*M* sulphuric acid is added. Then the mixture is heated just to boiling and cooled to room temperature (since the indicator used, ferroin, is unstable at higher temperatures) and then the unreacted excess iron(II) is titrated with standard cerium(IV) sulphate. Typical results of such experiments are shown in Table 4.

TABLE 4—DETERMINATION OF THALLIUM(III) AFTER REDUCTION WITH IRON(II) AT BOILING TEMPERATURE

Thallium(III) taken millimole	Iron(II) added millimole	Excess of Iron(II) millimole	Thallium(III) computed millimole	% error
0.2840	1.0000	0.4290	0.2855	+0.5
0.3550	1.0000	0.2852	0.3574	+0.7
0.4260	1.0000	0.1506	0.4247	−0.3
0.4970	1.5000	0.5000	0.5000	+0.6
0.5680	1.5000	0.3596	0.5702	+0.4
0.6390	1.5000	0.2132	0.6434	+0.7
0.7100	2.0000	0.5848	0.7076	−0.3
0.7810	2.0000	0.4272	0.7864	+0.7
0.8520	2.0000	0.2880	0.8560	+0.5

From the results in Table 4 it is evident that in most of the cases higher values are obtained. This is obviously due to atmospheric oxidation of iron(II) itself at higher temperature. In this connection it may be noted that Arthur John Berry[1] has recommended boiling in this method. From the results of the present authors shown in Table 4, it is clear that the method is inaccurate due to atmospheric oxidation. Hence the method needs the use of inert atmosphere for these determinations.

Though the former method gives accurate results it requires about half an hour for the reac-

TABLE 5—CATALYTIC EFFECT OF PHOSPHORIC ACID ON THE REACTION BETWEEN THALLIUM(III) AND IRON(II) AT ROOM TEMPERATURE

Time in minutes	Conc. of H_3PO_4 M	Thallium(III) taken millimole	Iron(II) added millimole	Excess of Iron(II) millimole	Thallium(III) computed millimole	% error
0	0	0	0.5000	0.5000	–	–
0	0.25	0	0.5000	0.5000	–	–
0	0	0.1400	0.5000	0.4900	0.0050	*
0	0.25	0.1400	0.5000	0.2300	0.1350	−3.6
1	0.25	0.1400	0.5000	0.2212	0.1394	−0.4
2	0.25	0.1400	0.5000	0.2194	0.1403	+0.2
3	0.25	0.1400	0.5000	0.2200	0.1400	nil
4	0.25	0.1400	0.5000	0.2208	0.1396	−0.3
5	0.25	0.1400	0.5000	0.2206	0.1397	−0.2
10	0.25	0.1400	0.5000	0.2200	0.1400	nil

* Almost no reaction.

tion to be completed between thallium(III) and iron(II) (especially when iron(II) is not too much in excess when compared with thallium(III) and the later method is inaccurate because of atmospheric oxidation. In view of these observations the present authors have attempted to use a catalyst which can make the reaction much faster. This can be achieved either by complexing iron(III) or thallium(I), one of the products of the present reaction. It is an established fact that phosphate ion is one of the complexing agents of iron(III)[7]. Moreover the formal redox potential[4] of thallium(III)-thallium(I) system in about 0.25M phosphoric acid will not be affected much when compared with its potential in sulphuric acid medium[4] alone. Hence phosphoric acid is chosen as a complexing agent for catalysing the reaction.

Indirect Determination of Thallium(III) after Reduction with Iron(II) in the Presence of Phosphoric acid as Catalyst at Room Temperature

Excess of iron(II) is added to thallium(III) to which sufficient amount of phosphoric acid is added, given some time and the excess unreacted iron(II) is titrated against standard cerium(IV) sulphate using ferroin as indicator (or potassium dichromate using diphenyl amine as indicator). The results of such experiments (Table 5) have shown that about 2.0 ml of syrupy phosphoric acid is sufficient for every 100 ml of the reaction mixture. From the table it is also clear that the reduction of thallium(III) with excess of iron(II) under such conditions is complete within a minute at room temperature.

Utilising the above conditions different amounts of thallium(III) are determined using both the oxidants (cerium(IV) sulphate and potassium dichromate) to titrate the excess unreacted iron(II). Typical results are given in Table 6.

TABLE 6—INDIRECT DETERMINATION OF THALLIUM(III) AFTER REDUCTION WITH IRON(II) IN THE PRESENCE OF PHOSPHORIC ACID AS CATALYST AT ROOM TEMPERATURE

Thallium(III) taken millimole	Iron(II) added millimole	Excess of Iron(II) millimole	Thallium(III) computed millimole	% error
Oxidant used – Ce(IV) ; Indicator used – Ferroin.				
0	0.4620	0.4620	–	–
0.0500	0.4620	0.3624	0.0498	−0.4
0.0750	0.4620	0.3124	0.0748	−0.3
0.1000	0.4620	0.2626	0.9970	−0.3
0.1250	0.4620	0.2116	0.1252	+0.2
0.1500	0.4620	0.1612	0.1504	+0.3
0.2000	0.6930	0.2950	0.1994	−0.3
0.2500	0.6930	0.1910	0.2510	+0.4
0.3750	0.9240	0.1760	0.3740	−0.3
0.5000	1.3860	0.3880	0.4990	−0.2
Oxidant used—Cr(VI) ; Indicator used—Diphenyl amine.				
0	0.4620	0.4620	–	–
0.0250	0.4620	0.4122	0.0249	−0.4
0.0500	0.4620	0.3622	0.0498	−0.2
0.0750	0.4620	0.3116	0.0752	+0.3
0.1000	0.4620	0.2626	0.0999	−0.1
0.1250	0.4620	0.2112	0.1254	+0.3

From the results in Table 6, thallium(III) can be determined within ±0.4% error using either cerium(IV) or chromium(VI) as oxidant. It needs neither inert atmosphere nor waiting for the completion of the reaction.

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Cation Exchange Separation of Iron, Cobalt and Nickel by Combined Ion Exchange Solvent Extraction Technique

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In the present paper, a method is described for the selective separation of iron, cobalt and nickel. The technique is based on the uptake of the metal ions on Amberlite IR-120, a strong acid cation exchange resin and then eluting with acetone-hydrochloric acid mixtures. The method can be successfully employed to separate the metal ions when present in milligram quantities. It is also possible to separate cobalt selectively in presence of other metal ions as cadmium, zinc, iron, nickel, etc.

WITH the introduction of combined ion exchange solvent extraction technique (CIESE), relatively great attention has been paid to the cation exchange studies and separation of various elements[1]. In most of the cases, acetone-hydrochloric acid mixture or tetrahydrofuran-hydrochloric acid mixture has been used as eluent. An effective separation of large amounts of iron(III) from cobalt, nickel and aluminium is possible using tetrahydrofuran-hydrochloric acid mixtures as eluents[2]. Korkisch et al have reported the selective separation of cobalt[3] and uranium[4] on a cation exchanger Dowex 50, X8. Acetone-hydrochloric acid mixtures have been used to separate calcium from copper, zinc, mercury(II), cadmium and iron[5], copper from nickel[6]. Distribution coefficients for 53 elements in 1.2 M HCl-water-acetone medium on Dowex 50, X12 resin have been reported by Peters and Del Fiore[7]. Strelow has reported separation of aluminium, gallium, indium and thallium by the CIESE technique[8]. Studies of nickel sorption from aqueous organic solutions of inorganic acids have been reported by Lastit, Alimarin and Belyavskaya[9].

Experimental

Reagents and Solutions

Stock solutions of metal ions used in the work were prepared by dissolving their AR grade salts in 3 N hydrochloric acid. In all the cases, the solutions prepared contained about 5 mg of metal ion/ml.

Solvent used was of reagent grade.

The acid cation exchanger, Amberlite IR-120 was used in the experiments. The column prepared had a height of about 22 cm and diameter 1.2 cm.

A stock EDTA solution (0.05 M) was prepared and standardized. For the determination of metal ions in eluate and in batch experiments (determination of distribution coefficients), EDTA titrations were performed following standard procedures.

Results

Determination of Distribution coefficients :

The distribution coefficients were determined by the batch equilibrium method[10]. Each equilibrium experiment was performed in 50 ml of mixture consisting of 0 or 40 to 90% acetone and 10 ml of 6 N hydrochloric acid and water up to 100%, and containing 5 mg of metal ion. The overall acidity of all the mixtures was 0.6 N hydrochloric acid. To the mixture, nearly 1 gm of dry resin was added and an equilibrium was set up by agitating the mixture on a shaking machine for eight hours. Resin was separated by filtration and filtrate was analysed quantitatively for the metal ion. The values of distribution coefficients for iron(III), cobalt(II) and nickel(II) are recorded in Table 1.

TABLE 1—DISTRIBUTION COEFFICIENTS OF IRON, COBALT AND NICKEL IN ACETONE-HCl MIXTURES

	Solvent mixture	Distribution coefficients		
		Fe(III)	Co(II)	Ni(II)
(1)	90% acetone+10% 6 M HCl	7	9	186
(2)	80% acetone+20% 3 M HCl	16	110	184
(3)	70% acetone+30% 2 M HCl	158	112	99
(4)	60% acetone+40% 1.5 M HCl	273	105	75
(5)	50% acetone+50% 1.2 M HCl	156	101	211
(6)	40% acetone+60% 1 M HCl	150	175	161
(7)	0.6 M HCl	117	28	80

An experimental error of the measurement of distribution coefficient was observed. It was about 10%. The values obtained above in different solvent systems can be interpreted in terms of the separation factor (Ka). Higher the deviation of separation factor from one, higher is the selectivity and simpler are the conditions of separation. From Table 1 it is clear that Fe(III) has distribution coefficient of 16 in 80% acetone-HCl mixture as compared to 110 for Co(II) and 184 for Ni(II). This means on elution with 80% acetone-HCl mixture, the least strongly adsorbed ion on the

resin will be Fe(III) while Co(II) and Ni(II) will be retained on the resin. Fe(III) will be washed out first but Co(II) and Ni(II) will remain adsorbed. Once Fe(III) is removed, Co(II) and Ni(II) can then be separated by eluting with 90% acetone-HCl mixture. The values of distribution coefficients in this solvent mixture have large difference. On washing the column with this mixture, will selectively elute least adsorbed Co(II) while Ni(II) will be retained. Finally Ni(II) can be washed out with 0.6 *M* HCl. *It is also concluded from the values of distribution* coefficients that only these three solvent systems can be satisfactorily used for separation purpose.

Separation of iron, cobalt and nickel

The resin column was prepared and it was first washed with 80% acetone-HCl mixture. The volume used was 100 ml. Twenty ml of mixture of Fe(III), Co(II) and Ni(II) in 3*N* HCl was taken and to it 80 ml of acetone were added. This solution (which is now 80% in acetone and 20% in 3*N* HCl) was passed through the column at a flow rate of 1 ml/minute. 200 ml more of the solution (80% acetone-HCl) were passed through the column at the same flow rate. This quantitatively eluted out iron. Cobalt was next separated with 90% acetone-HCl mixture, 150 ml of this eluent were required for complete elution of cobalt. The cobalt eluate was deep blue in colour. Finally nickel was separated by washing with hydrochloric acid. The concentrations of iron, cobalt and nickel in the solutions were determined volumetrically by EDTA titrations.

Table 2 below shows the results obtained in typical separations.

TABLE 2—SEPARATION OF Fe(III), Co(II) and Ni(II) ON AMBERLITE IR-120

	Metal ion taken (mg)	Found (mg)	Per cent. recovery
(1)	Fe – 13.16	13.16	100
	Co – 7.36	7.65	103.9
	Ni – 10.57	10.25	96.9
(2)	Fe – 22.35	22.12	98.9
	Co – 10.90	11.12	102.1
	Ni – 15.86	15.54	97.9

Presence of other elements

The presence of the following elements in the separation process was studied, Cu(II), Zn(II), Mg(II), Cd(II) and Al(III). The distribution coefficients of these metals in 80%, 90% acetone-HCl mixtures and in HCl alone were determined. The values obtained are recorded below in Table 3.

TABLE 3—VALUES OF DISTRIBUTION COEFFICIENTS

Solvent mixture	Distribution coefficients				
	Cu(II)	Zn(II)	Mg(II)	Cd(II)	Al(III)
80% acetone-HCl	3	1	164	1	230
90% acetone-HCl	1	1	86	5	230
0.6 *M* HCl	2	33	30	17	185

Mixture containing 10 mg each, of these metal ions and Fe, Co and Ni was prepared. Separation was followed using 80% acetone-HCl and 90% acetone-HCl and HCl solutions. The first eluate contained the following metal ions Fe, Cu, Zn, Cd. Second eluate contained Co only while in nickel fraction, Mg and Al got eluated. The values of distribution coefficients also support the observations.

From the results obtained in the studies, it is seen that the selectivity of separation of cobalt from other elements in acetone-HCl medium is far greater than in pure hydrochloric acid solution. Separation of cobalt from Cu(II), Zn(II), Mg(II) and Cd(II) using HCl alone as eluent is not possible because of similarity of distribution coefficients. For trivalent ions as Fe(III), Al(III) large quantities of resin are required for separation. These limitations can be overcome in acetone-HCl systems and cobalt can be selectively separated from the elements listed in Table 3.

A quantitative separation of cobalt from these elements was achieved. Table 4 below shows the results obtained.

TABLE 4—SELECTIVE SEPARATION OF COBALT AMOUNT OF COBALT TAKEN=6.93 mg

Other ion present, mg		Amount of Co recovered, mg	Per cent. recovery
Ni(II)	10	6.93	100
Mg(II)	10	6.69	96.53
{Ni(II), Mg(II)}	15, 15	6.628	96
Cu(II)	10	6.93	100
Zn(II)	10	6.93	100
{Mg(II), Cu(II), Zn(II)}	10, 10, 10	6.80	98.12

The experiments were done using 5 to 50 mg of cobalt and varying amounts of other metal ions. After selective separation of cobalt, quantitative recovery of the elements is also possible.

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Kinetics of Oxidation of Cyclic Alcohols by Acid Bromate

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The oxidation of cyclic alcohols with common rings (five, six and seven membered) by bromate has been studied in binary solvent mixture of acetic acid and water in the presence of sulphuric acid. The reaction is first order each in the substrate and the oxidant, and second order with respect to sulphuric acid. The rate of the reaction increases with increase in sulphuric acid concentration. The reaction was found to follow free radical mechanism. The order of the reactivity of the alcohols is cyclopentanol < cyclohexanol < cycloheptanol, which is in conformity with Bayer strain theory. Increasing the acetic acid content of the medium the rate increases, and the reaction has been described as an ion-dipole reaction.

THE oxidation of cyclic alcohols have been studied with different oxidants like Vanadium(V)[1], Ce(IV)[2] and Cr(VI)[3] in acid medium and with hexacyanoferrate(III)[4] in basic medium. But no work seems to have been done on oxidation of cyclic alcohols with bromate ion. Though potassium bromate is a powerful oxidising agent with oxidation potential 1.4 volts in acid medium, it was used as a source of Br_2 in presence of Br^- ion. In the present study of bromate oxidations, the product Br^- ion formed in the reaction mixture reacts with Br(v) to generate bromine which on accumulation oxidises the substrate along with bromate ion. Hence to eliminate bromine oxidation, which is much faster than the oxidation by bromate ion, the product bromide ion has been suitably complexed as soon as it is formed, by use of mercuric acetate.

In continuation of our earlier work on the oxidation of phenols by bromate[5] we are communicating in this report the results of pure bromate oxidation of cyclic alcohols with common rings (five, six and seven membered) at various temperatures in the range 40-60° and in various amounts of acetic acid as solvent. The experimental details are given in our earlier paper[5].

Results and Discussion

The order of reactivity for the cyclanols (Table 1) is cyclopentanol < cyclohexanol < cycloheptanol which is in ascending order of ring size, is in conformity with Bayer strain theory but not with I strain hypothesis. This order is different from the orders found in V(V), Ce(IV) and Cr(IV), where the interpretation was suggested on the basis of I strain hypothesis. This ascending order of ring size was also found in the oxidation of alcohols by hexacyanoferrate(III) in basic medium[4].

The reactivity of cyclohexanol can be explained by assuming that it is reacting through its flexible boat form rather than the chair form, because chair form is more stable. In the boat form there is no angle strain but there is bond opposition strain, involving four pairs of hydrogens at the side of the boat and also the strain due to the pair of hydrogens at the top of the boat known as the bowspritflagpole interaction[6]. As a result of these interactions the boat form is less stable than the chair form.

The reaction is first order in oxidant and substrate and second order with respect to sulphuric acid. The rate was found to be increased on increasing sulphuric acid studied in the range 0.1*M* to 1.0*M* and it was observed log *k* against *p*H was linear with slopes of 1.8 to 2.0. The reactions were studied with different percentages of acetic acid, (Table 2) and plot of log *k* against 1/D was linear

TABLE 1—EFFECT OF SULPHURIC ACID ON THE RATE OF REACTION

$(BrO_3^-) = 5 \times 10^{-3} M$; (cyclanol) $= 5 \times 10^{-2} M$; $[Hg(CH_3COO)_2] = 0.01 M$

Acetic acid = 40% ; Temperature = 30°

$k \times 10^{4}\ lm^{-1}s^{-1}$

$(H_2SO_4)/M$	0.2	0.4	0.6	0.8	1.0
Cyclopentanol	0.58	1.62	3.21	5.13	8.56
Cyclohexanol	0.75	2.32	5.12	10.2	12.6
Cycloheptanol	0.64	2.70	6.08	12.1	20.5

TABLE 2—EFFECT OF ACETIC ACID ON THE RATE OF REACTION

$(BrO_3^-) = 5 \times 10^{-3} M$; (Cyclanol) $= 5 \times 10^{-2} M$; $[Hg(CH_3COO)_2] = 0.01 M$

$(H_2SO_4) = 0.4 M$; Temperature = 30°

$k \times 10^{4} lm^{-1}s^{-1}$

% Acetic acid	10	20	30	40	50
Cyclopentanol	0.33	0.46	0.63	1.62	4.05
Cyclohexanol	0.42	0.74	1.26	2.32	6.39
Cycloheptanol	0.53	0.90	1.42	2.70	7.33

with a positive slope indicating that the reaction is between a cation and a dipole. The cation should be the protonated bromate ion $H_2BrO_3^+$ which is in consistance with order being two with respect to hydrogen ions.

The reaction was studied at different concentration of substrate (Table 3). The slopes of log k_{obs} vs. log (cyclanol) were not strictly unity. The data also yield linear plots of $1/k_{obs}$ vs. 1(/cyclanol) with definite intercept indicating the formation of cyclanol-bromate complex and also suggesting that rate expression is of the form,

$$\frac{-d[Br(V)]}{dt} = Kk\ [ROH]\ [Br(v)]/1 + Kk\ [ROH]$$

where K is the equilibrium constant for the formation of alcohol-bromate complex and k is the disproportionation constant of the complex.

TABLE 3—EFFECT OF CYCLANOL ON THE RATE OF REACTION

$(BrO_3^-) = 5 \times 10^{-3} M$; $(H_2SO_4) = 0.4 M$; Acetic acid = 40%

$[Hg(CH_3COO)_2] = 0.01 M$; Temperature = 30°

$k \times 10^3$ min^{-1}

(Cyclanol)/M	0.05	0.10	0.15	0.20	0.25
Cyclopentanol	4.85	9.60	13.20	17.06	23.08
Cyclohexanol	6.95	14.00	19.19	25.60	31.62
Cycloheptanol	8.10	15.98	20.51	26.71	33.77

The oxidation was studied in the temperature range 40-60° and the activation energies for cyclopentanol, cyclohexanol and cycloheptanol were 18.3, 14.1 and 16.6 K cal respectively. The products of oxidation were found to be corresponding cyclic ketones and bromide ion. The ketones were identified by comparing the m.p. of their 2,4-DNP derivatives with the authentic samples. The formation of Br^- ion was confirmed by the addition of $AgNO_3$ to the reaction mixture. Free radicals were detected in the system by the addition of acrylonitrile and acrylamide.

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On the Determination of Solution Moment of a Solute

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Earp and Glasstone theory[3] on the dielectric polarization of binary mixtures has been discussed theoretically to understand the merits of the proposed equation by Earp and Glasstone. An attempt is made to modify Earp and Glasstone method without violating the very purpose of their suggestions. Validity of the modified relation is discussed with the study of dielectric polarization of Phenol, Ethyl acetate and Chlorobenzene in benzene.

THE method of dielectric polarization measurements in binary mixtures of a polar solute in a polar/non-polar solvent is extensively adopted not only for studying the electrical aspects of molecular behaviour, but also for tracing the possible existences of molecular interaction and the extent of electronic perturbations by the influences of neighbouring molecules[1-3]. Considering the case of a mixture of components X and Y, Earp and Glasstone[3] pointed out the possibility of formation of additive compound XY, what is known as loose complex, in which a definite linkage is formed. The dioxane effect[4-6] and the detailed study of molecular conformation of such loose complexes[7-10] have led to understand the degree of electronic perturbation and the classification of solute-solvent interaction to some extent. The purpose of this paper is to explore further a simple approach to molecular polarization of a polar solute tn a polar/non-polar solvent at infinite dilution.

Experimental

The apparatus and methods used were as previously described[11]. Each compound was purified by standard methods immediately before its dipole moment was determined.

Theoretical Considerations :

Earp and Glasstone theory[3] implies that the total polarization of a binary mixture, in general, varies linearly with the square of volume polarization and it was reasonably concluded that it indicates the absence of chemical interaction between the components of the solution[3,12,13]. According to Earp and Glasstone, the molar polarization of mixtures can be expressed by the following expression.

$$P_{12} = A + B\left[\frac{\epsilon_{12}-1}{\epsilon_{12}+2}\right]^2 \quad \dots (1)$$

where P_{12} is the molar polarization of the mixture, ϵ_{12}, the dielectric constant of the mixture and A and B are constants for a given solute and solvent, the value of which, by considering the polarization of mixtures is a linear function of its excess of square of volume polarization over that of the solvent, can be shown as,

$$B = \frac{P_2 - P_1}{\left(\frac{\epsilon_2-1}{\epsilon_2+2}\right)^2 - \left(\frac{\epsilon_1-1}{\epsilon_1+2}\right)^2} \quad \dots (2)$$

and

$$A = P_1 - B\left(\frac{\epsilon_1-1}{\epsilon_1+2}\right)^2 \quad \dots (3)$$

where ϵ_1 and ϵ_2 are the dielectric constants of solvent and solute having molecular polarization P_1 and P_2 respectively. From these relations one can obtain for the molecular polarization of solution as

$$P_{12} = P_1 + \frac{(P_2 - P_1)(\epsilon_2+2)^2}{(\epsilon_2-\epsilon_1)} \left[\frac{\Delta\epsilon(5\epsilon_1 - 3\epsilon_{12} + 2\epsilon_{12}\epsilon_1)}{(\epsilon_{12}+2)^2(5\epsilon_1 - 3\epsilon_2 + 2\epsilon_1\epsilon_2)}\right] \quad \dots (4)$$

where $\Delta\epsilon = \epsilon_{12} - \epsilon_1$, the excess of dielectric constant of the mixture over that of the solvent. Under the assumption of an 'ideal mixture condition by keeping the molecular polarization of the solvent molecule invariant, equal to the value for the pure liquid, the apparent polarization of solute molecule can be easily computed.

In most cases Earp and Glasstone method (EGM) leads to higher values of molar polarization than that of the experimentally observed values using the relation[14].

$$P_{12} = \frac{\epsilon_{12}-1}{\epsilon_{12}+2} \cdot \frac{M_1 f_1 + M_2 f_2}{d_{12}} \quad \dots (5)$$

It implies that Earp and Glasstone theory needs some modifications. An attempt is made to modify their relation without violating the very purpose of Earp and Glasstone method.

Considering chemically non-interacting systems, it is well noted that the effective molar polarization P_{12} of dilute solution in polar/non-polar solvents

shows linearity to the excess volume polarization over that of the solvent. By adopting a similar procedure, the effective molar polarization of dilute binary mixtures may be expressed as

$$P_{12} = P_1 + \frac{(P_2 - P_1)(\epsilon_2 + 2)}{(\epsilon_2 - \epsilon_1)}\left[\frac{\Delta\epsilon}{\epsilon_{12} + 2}\right] \quad \ldots \quad (6)$$

From the knowledge of concentration dependance of the apparent molar polarization for the solute, the molar polarization of the solute at infinite dilution can be obtained by extrapolation and the dipole moment μ (in Debye Unit) of the solute molecule can be computed from the usual expression.

$$\mu = 0.01281\sqrt{(P_2 - R_D)T} \quad \ldots \quad (7)$$

where R_D is the molar refraction of the solute for the sodium *D line* and T is the temperature of measurement in degrees absolute.

Results and Discussion

With a view to examine the merits of the proposed equation, the study of dielectric polarization of Phenol, Ethyl acetate and Chlorobenzene in benzene, though studied earlier, has been undertaken. The results are given in Tables 1 to 3. The values of molecular polarization at infinite dilution and the dipole moment for the solutes studied here are reported in Table 4. To compare the dipole moment the values taken from the "Tables of Experimental dipole moments"[15] are used.

It is well known that the dielectric constants of binary mixtures are not usually equal to the calculated average values[16]. The molar polarization of solute molecule in solvent usually increases at *infinite* dilution and this can be taken as an indication for the complexing tendency of solute molecule with solvent molecule. When there is absolutely no interaction between solute and solvent molecules, the curve ϵ_{12} vs f_2, the mole fraction of solute should be linear. This leads to

$$P_{2\infty} = P_1 + (P_2 - P_1)\frac{\epsilon_2 + 2}{\epsilon_1 + 2} \quad \ldots \quad (8)$$

This is very similar with the empirical relation proposed for a system where strong or specific interactions are absent[17]. It is found that the range of validity of the reported relation for a quick determination of dipole moment in solution has got certain limitations over the range of dielectric constant of solute. This limitation may be due to the following reasons :

(i) the opposing atmosphere of dipoles due to the non-symmetrically distributed interacting electrons about the atomic nuclei[18],

(ii) the intra and inter molecular interactions in the solute molecules,

(iii) the existence of single and double ionic structure of molecules.

The critical examination of this equation[19] shows that equation (8) is in unison with the above predictions.

TABLE 1—PHENOL-BENZENE BINARY SYSTEM

$\epsilon_1 = 2.2750$ $P_1 = 26.7450$ c.c. $R_D = 28.14$

$\epsilon_2 = 9.6840$ $P_2 = 72.7807$ c.c.   T = 298K

$100f_2$	ϵ_{12}	$\left[\frac{\Delta\epsilon}{\epsilon_{12}+2}\right]$	$\left[\frac{\Delta\epsilon}{(\epsilon_{12}+2)f_2}\right]$	P_{12} Modified EGM	P_{12} EGM	$P_{2\,app}$ Modified EGM	$P_{2\,app}$ EGM
0.2460	2.2831	0.0019	0.772	26.883	26.954	82.79	111.66
0.4260	2.2895	0.0034	0.798	26.992	27.121	84.21	115.08
0.6720	2.2998	0.0057	0.849	27.159	27.388	88.37	122.41
0.7090	2.3012	0.0061	0.862	27.188	27.428	89.80	122.43
0.8150	2.3060	0.0072	0.883	27.268	27.548	90.86	125.34
0.9476	2.3120	0.0086	0.908	27.369	27.699	92.63	127.54

TABLE 2—ETHYL ACETATE-BENZENE BINARY SYSTEM

$\epsilon_1 = 2.2750$ $P_1 = 26.7450$ c.c. $R_D = 17.61$

$\epsilon_2 = 6.6721$ $P_2 = 52.8680$ c.c.   T = 298K

$100f_2$	ϵ_{12}	$\left[\frac{\Delta\epsilon}{\epsilon_{12}+2}\right]$	$\left[\frac{\Delta\epsilon}{(\epsilon_{12}+2)f_2}\right]$	P_{12} Modified EGM	P_{12} EGM	$P_{2\,app}$ Modified EGM	$P_{2\,app}$ EGM
1.9891	2.3578	0.0190	0.955	27.723	29.092	75.98	94.47
3.0248	2.3909	0.0264	0.875	28.104	28.608	81 81	88.34
6.9236	2.5396	0.0583	0.842	29.747	30.786	70.11	85.11
8.8598	2.5988	0.0704	0.812	30.371	31.582	68.56	82.60

TABLE 3—CHLOROBENZENE-BENZENE BINARY SYSTEM

$\epsilon_1 = 2.2750$ $\quad P_1 = 26.7450$ c.c. $\quad R_D = 32.85$

$\epsilon_2 = 5.6212$ $\quad P_2 = 61.7880$ c.c. $\quad T = 298K$

$10 f_2$	ϵ_{12}	$\left[\frac{\Delta\epsilon}{\epsilon_{12}+2}\right]$	$\left[\frac{\Delta\epsilon}{(\epsilon_{12}+2)f_2}\right]$	P_{12} Modified EGM	P_{12} EGM	P_2 app Modified EGM	P_2 app EGM
0.2758	2.3533	0.0160	0.655	28.181	28.626	79.02	94.92
0.6458	2.4878	0.0367	0.568	29.674	30.586	72.08	85.45
0.8391	2.4783	0.0454	0.541	30.368	31.414	69.92	82.39
1.1053	2.5027	0.0508	0.460	30.800	31.992	68.46	78.67
1.3662	2.5430	0.0590	0.432	31.454	32.768	61.22	70.83
1.6192	2.5692	0.0644	0.398	31.885	33.298	58.51	67.21

TABLE—4

Solute	$\left[\frac{\Delta\epsilon}{(\epsilon_{12}+2)f_2}\right]_{f_2\to 0}$	$P_{2\infty}$ c.c.	μ	μ other values from literature*
Phenol	0.74	80.47	1.60	1.60
Ethyl acetate	1.05	80.62	1.75	1.77
Chlorobenzene	0.73	85.06	1.59	1.58

μ values are expressed in Debye units.
* Reference (15).

With a rough approximation, the modified relation explains Higashi equation[20], proposed for a quick determination of electric dipole moment of a molecule. According to Higashi,

$$\mu = S.\sqrt{\left(\frac{\Delta\epsilon}{f_2}\right)_{f_2\to 0}} \quad \cdots \quad (9)$$

where S is a constant characteristic of the solvent. For benzene Higashi gave a value of 0.9) with a possible fluctuation of ±0.I0 e.s.u., With an assumption that at very low concentration $\epsilon_{12}+2 \simeq \epsilon_1+2$ and by neglecting $P_1 - R_D$, one can get,

$$S = 0.01281\left[\frac{(P_2-P_1)(\epsilon_2+2)}{(\epsilon_2-\epsilon_1)(\epsilon_1+2)}T\right]^{\frac{1}{2}} \quad \cdots \quad (10)$$

The characteristic values of S have been determined from the equation (10). The calculated values are 0.94 for Phenol, 0.77 for Ethyl acetate and 0.95 for Chlorobenzene and are more or less in close agreement with Higashi's proposed value 0.90±0.10.

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Ferrous-Chlorate Redox System as Initiator of Aqueous Vinyl Polymerization

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Ferrous – Chlorate redox system is a very powerful initiator for the aqueous polymerization of a number of vinyl monomers. With methylmethacrylate, polymerization takes place even in the presence of atmospheric oxygen giving nearly 70% conversion. Endgroups incorporated are hydroxyl and chlorine totalling to an average of one to one and half per chain. Based upon these findings a suitable mechanism of initiation has been proposed.

IN a past communication[1] the author has shown that ferrous-bromate redox is a very efficient redox initiator for aqueous vinyl polymerization. In this communication some results of the aqueous polymerization of vinyl monomers, particularly methylmethacrylate by ferrous-chlorate redox system are reported.

Experimental

The monomers from B. D. H. or E. Merck were purified by the usual procedures and stored in a refrigerator. All other reagents were analytical grade products from either E. Merck or B.D.H. and were used without further purification. A stock solution of $0.1M$ Ferrous sulfate in $0.1M$ sulfuric acid was prepared.

Aqueous polymerization of purified monomers was carried out in pyrex conical flasks at ambient temperature ($\simeq$30°) under N_2-atmosphere. Polymerization started immediately after the reactants were mixed with no or a little induction period and proceeded through a sol to a coagulated phase. The reaction was allowed to continue till maximum conversion was obtained or terminated after a definite time by the introduction of hydroquinone. The polymers obtained were filtered, washed several times with distilled water and finally dried in an air even at 45°. The polymer yield, where necessary, was measured gravimetrically.

Some of the dried samples were purified by the usual method of repeated precipitation[2] and were then subjected to the dyepartition test[3] for characterization of the endgroups incorporated in them. Hydroxyl endgroups (after their chemical transformation to sulfate endgroups) were detected and estimated with the help of methylene blue dye reagent[4] and halogen endgroups (after their transfomation into dye responsive quaternary haliderendgroups) with disulfine blue dye reagent[5]. For measurements of the optical density of the developed colour a Hilger spectrophotometer was used.

Viscosity measurements of the polymer samples in benzene solution were carried out at 30±0.1° using an Ubbelohde suspended level viscometer and number average molecular weight ($\overline{M}_n$) was obtained from the intrinsic viscosity [η] from the relation[6] $[\eta]=8.69\times10^{-5}\times(\overline{M}_n)^{.76}$

Results and Discussion

Monomer selectivity: Almost all the water soluble vinyl monomers are polymerized with Fe^{+2}-ClO_3^- redox initiator. The initiator system readily initiates the polymerization of methylmethacrylate, ethylmethacrylate, ethyl acrylate and methyl acrylate in acid aqueous media with no or a little induction period. The maximum conversion is between 60-80% in these cases. Styrene is polymerized only after a prolonged induction period and a low yield of polymer is obtained probably due to its limited solubility in water. Acrylamide and acrylonitrile are also polymerized by this initiator system which, however, fails to initiate the polymerization of acrylic acid and methacrylic acid. The results of polymerization of different monomers are shown in Table 1. % Conversion of monomers into polymers in two hours gives an idea of the relative rates of polymerization of these monomers. For further studies, methylmethacrylate (MMA) has been chosen as the monomer, because it polymerizes with highest rate, gives highest yield of polymer with a higher [η] and polymethylmethacrylate (PMMA) can be easily purified by the usual method.

Effect of Oxygen: In all polymerization experiments dissolved oxygen of water was removed by flushing through purified nitrogen for ten minutes

TABLE 1—AQUEOUS POLYMERIZATION OF VINYL MONOMERS USING Fe^{+2}-ClO_3^- REDOX

[Monomer]=0.1*M*, $[ClO_3^-]=5\times10^{-3}M$, $[Fe^{+2}]=1\times10^{-3}M$

Temperature≅30°

Monomer	Induction period in minutes	% Conversion in 2 hours	[η]
Methylmethacrylate	Nil	65	2.09
Ethylmethacrylate	2	61	1.98
Ethylacrylate	4	36	1.48
Methylacrylate	2	39	1.68
Styrene*	130	18	1.78
Acrylonitrile	12	27	1.32
Acrylamide	16	35	1.57
Acrylic acid	No polymerization		
Methacrylic acid	"		
Vinyl acetate	"		

* Only 0.02*M* solution was used because of its limited solubility in water.

before adding the reactants. The induction period depends upon the rapidity of removal of traces of oxygen still present in the reacting solution by the reactive species generated by the initiating system and consequently on its concentration and efficiency. Using even a very low initiator concentration, a little or almost no induction period was observed for MMA polymerization. Particularly for this monomer the system is so efficient that polymerization starts within a few minutes even if the non-deaerated reaction mixture is left open to atmosphere, and limiting conversion is about 70%.

Polymer endgroups : Results of endgroup analysis of PMMA samples are shown in Table 2. Polymer samples have been prepared using a wide range of initiator concentrations in acid aqueous media. The *p*H of the aqueous media was maintained by sulfuric acid. The expected halogen and hydroxyl endgroups have been detected and estimated. Halogen endgroup content is between 0.64 to 1.23 and hydroxyl endgroup content between 0.27 to 0.38 per polymer molecule. On the average the total endgroup content per polymer molecule is between 1 and 1.5. Compared with Fe^{+2}-BrO_3^- initiator system[1], the present initiator system incorporates more halogen bearing endgroup and less hydroxyl endgroup and also the total functional endgroup content is a little higher. *p*H of the reaction media is found to have no appreciable influence on the endgroup profile and [η] of the polymers.

TABLE 2—ENDGROUP PROFILE OF PMMA OBTAINED BY INITIATION WITH Fe^{+2}-ClO_3^- SYSTEM IN AQUEOUS MEDIUM. [MMA]=0.094 *M*, N_2-ATMOSPHERE, TEMPERATURE≅30°

$[Fe^{+2}]$ $M\times10^3$	$[ClO_3^-]$ $M\times10^3$	*p*H	[η]	Endgroup/Chain		
				halogen	hydroxyl	Total
2.5	5.0	3.4	2.48	1.14	0.38	1.52
7.5	5.0	3.4	1.85	0.66	0.27	0.93
25.0	5.0	3.4	1.12	0.87	0.36	1.23
100.0	5.0	3.4	0.69	0.78	0.33	1.11
7.5	20.0	3.4	0.98	1.07	0.27	1.34
7.5	100.0	3.4	0.55	1.23	0.31	1.54
7.5	5.0	3.1	1.80	0.70	0.32	1.02
7.5	5.0	2.3	1.88	0.64	0.28	0.92
7.5	5.0	1.4	1.76	0.67	0.33	1.00

Mechanism : That the polymerization is completely inhibited by hydroquinone or D. P. P. H. (diphenyl picryl hydrazyl radical) clearly indicates the free radical nature of the reaction. Since both chlorine and hydroxyl endgroups have been incorporated in the polymers, these must have been formed in the medium in the form of radicals during the reduction of ClO_3^- by Fe^{+2} as suggested by Gleason, Mino and Thomas[7] and have taken part in the initiation step. Further, Firsching and Rosen[8] who found halogen and sulfur bearing endgroups in ClO_3^--SO_3^{-2} initiated polymers suggested that chlorine catalyst enters the polymer during hypochlorite reduction to chloride. In view of our endgroup results and the suggestion of Firsching and Rosen[8], the following initiation steps may be suggested.

$$Fe^{+2}+ClO_3^-+H^+\rightarrow Fe^{+3}+ClO_2^-+\dot{O}H \quad \ldots \quad (1)$$

$$Fe^{+2}+ClO_2^-+H^+\rightarrow Fe^{+3}+ClO^-+\dot{O}H \quad \ldots \quad (2)$$

$$Fe^{+2}+ClO^-+H^+\rightarrow Fe^{+3}+\dot{C}l+\bar{O}H \quad \ldots \quad (3)$$

$$\text{or } Fe^{+3}+\bar{C}l+\dot{O}H$$

The chlorine atom may also be generated in the reaction medium by the radical transfer reaction[9] of OH radicals with the end product Cl^- ions.

$$\dot{O}H+\bar{C}l\rightarrow\bar{O}H+\dot{C}l \quad \ldots \quad (4)$$

If only step (3) produces the initiating radical, then this initiator system becomes equivalent to Fe^{+2}-Cl_2 initiator[10] which initiates polymerization by a step similar to (3). That this is not the case is demonstrated by the fact that Fe^{+2}-ClO_3^- system polymerizes MMA many times faster than it is polymerized by Fe^{+2}-Cl_2 system. The present initiator system produces more halogen bearing endgroups in the polymers compared with Fe^{+2}-BrO_3^- system which suggests that chlorine atom is a better polymerization initiator than bromine atom.

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Influence of Moisture on the Electrical Conductance of Lead Nitrate Crystals

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The influence of moisture on the electrical conductance of lead nitrate has been investigated. It has been observed that the conductance increases with the relative humidity of the environment. A mechanism involving adsorption, absorption, diffusion and ionization has been suggested to explain the effect.

SEVERAL studies have been made by various workers on the ionic conductivity of inorganic crystals particularly the alkali metal halides and it has been accepted generally that the conductance of crystals is ordinarily due to the motion of free positive ion vacancies having an apparent negative charge[1]. The positive ion vacancies are considerably mobile and the conductance of the crystal can be considered as a direct measure of the number of positive ion vacancies.

It has also been observed that the conductance of potassium bromide and potassium iodide increases in the presence of bromine and iodine vapours respectively[2]. The fact that water can penetrate rock salt has been confirmed by infrared absorption spectrum[3]. A number of workers have observed slow sorption processes for the following systems[4] : sulphur dioxide in sodium chloride, hydrogen chloride in potassium chloride, and ammonia in sodium chloride.

During the course of some of the investigations on the electrical conductance of lead nitrate crystals in this laboratory it has been observed that traces of moisture produce appreciable effect on the conductance of the system. It was, therefore, of interest to investigate in detail the influence of moisture on the electrical conductance of lead nitrate crystals and the present study was undertaken.

Experimental

Analytical reagent grade (E. Merck) lead nitrate was used for the investigations. Crystals of lead nitrate in the form of tablets (diameter, 6 mm ; length 5-7 mm) prepared under a pressure of 20 tons per square inch with an Amsler machine (Alfred J. Amsler & Co., Switzerland) and a steel die were used for conductance measurements. The samples were held under pressure by two loaded springs between brass discs covered with platinum foil which served as electrodes. The surfaces in contact with the electrodes were painted with Conductive Silver Composition 4817 (E.I. du Pont de Nemours & Co., U.S.A.) for better electrical contact. A microammeter (Model No. 350, Taylor Electrical Instruments Ltd., Slouch, Bucks., England) was used to measure the conductance of the samples. Ohm's law was obeyed and no polarization effects were observed.

To study the influence of moisture on the electrical conductance of lead nitrate, the conductance was measured by keeping the samples in various humidity-controlled atmospheres for periods up to 24 hr, by which time a state of equilibrium was attained. The constant humidity-controlled environments were obtained by taking mixtures of sulphuric acid and water in the proportions[5] (in terms of density) given below :

Density of sulphuric acid-water mixture	Relative humidity, per cent.
1.1	93.9
1.15	88.8
1.2	80.5
1.25	70.4
1.3	58.3

The samples for conductance measurements were placed over these mixtures in desiccators.

To start with, the conductance of the tablet after desiccating it over phosphorus pentoxide in a desiccator for 48 hr. was measured. The sample was then transferred and kept over the sulphuric acid-water mixture taken in a desiccator, the connecting wires were taken out through the hole in the wall of the desiccator, the hole being sealed air tight with sealing wax. The conductance of the sample was then measured. The tablet was allowed to remain in the constant relative humidity atmosphere in the desiccator and its conductance was measured at 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 15, 20 and 24 hr. It was then desiccated thoroughly over phosphorus

pentoxide and then used for conductance measurements in another humidity-controlled atmosphere as before. A constant potential of 12 volts, d.c., was applied for the measurements.

Results

Data on the influence of moisture on the electrical conductance of lead nitrate are presented graphically in Fig. 1. For a given relative humidity

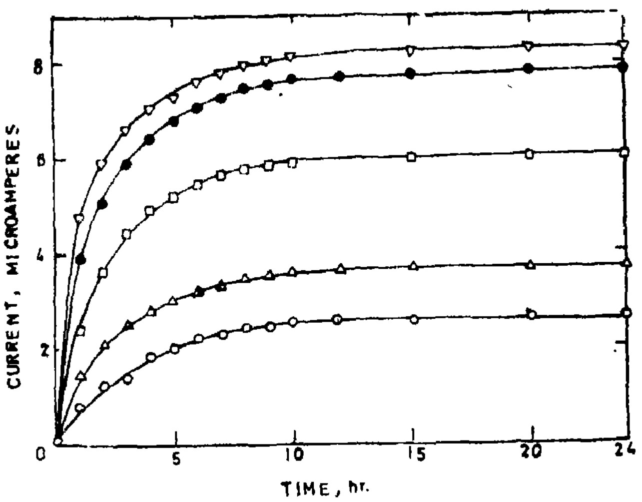


Fig. 1. Variation of conductance with time.

○ RH 70.4
△ RH 80.5
□ RH 85.0
● RH 88.0
▽ RH 93.9

there is a rapid rise in the electrical conductance in the beginning, up to 10 hr., and then slows down monotonically. For example, at a relative humidity of 85.0 per cent. the current at 0 hr. is 0.05 microampere and 5.2 after 5 hr., 5.95 after 10 hr. whereafter it becomes steady over a period of 24 hr. It is of interest to note that the rate of increase is greater at higher relative humidities of the environment.

Discussions

The current-time relationships represented in Fig. 1 are similar to those obtained by Mc Bain[6] for the adsorption of iodine by carbon where the rate of adsorption is very high at first but drops off fairly steeply after the first few minutes. It is evident from these plots that the rate of increase is very high at first, up to 10 hr., and then almost a constant for a period of 24 hr. The similarity of these plots with those of Mc Bain[6] suggests that the mechanism involved in both the cases is similar. Saturation curves similar to that obtained here have been obtained by Tryhorn and Wyatt[7] for the adsorption of vapours of pure liquids, viz. CH_3OH, CS_2, $(CH_3)_2CO$, H_2O, $CH_3COOC_2H_5$ and C_2H_5I, on coconut charcoal.

Bangham and Burt[8] have observed that the time relationship of adsorption of gases by solids obey the simple law

$$S^m = kt \qquad \ldots (1)$$

where S is the amount of adsorption up to the time t after admission of gas and m is a constant which may have a value as high as 12 depending on various factors. Herbert[4], and Bangham and Burt[8] have also observed similar relationship to hold good for adsorption of SO_2 and NH_3 respectively.

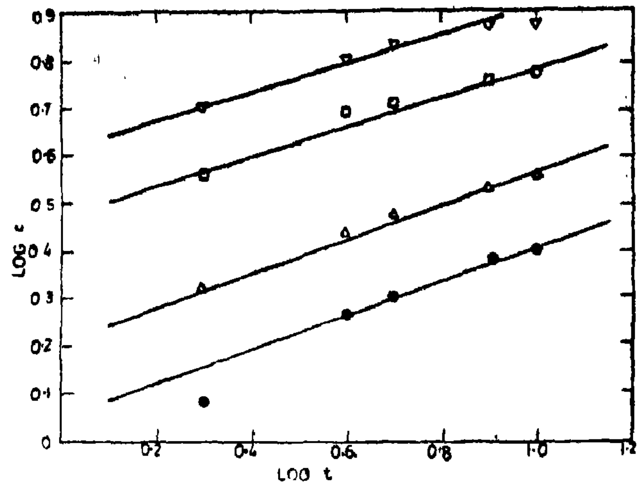


Fig. 2. Variation of log c with log t.

● RH 70.4
△ RH 80.5
□ RH 85.0
▽ RH 88.6

In Fig. 2 are plotted logarithm of the equilibrium current against logarithm of time of exposure of the sample to moisture up to 10 hr. during which period a steady state of equilibrium has been established as indicated by the plots in Fig. 1. The linear plots in Fig. 2 show that an equation of the type

$$c^m = kt \qquad \ldots (2)$$

where c is the equilibrium current, holds good. Therefore it is possible that the process involved is one of adsorption. The plots in Fig. 2 are parallel with $m = 0.44$ in agreement with the above equation and the classical Freuendlich adsorption isotherm.

Davis[9] has shown that adsorption is invariably followed by absorption. The water vapours that are adsorbed by the crystals are therefore absorbed and pass into the interior of the crystals. Studies on the conductance of potassium bromide and potassium iodide in the presence of bromine and iodine vapours respectively have revealed that the conductance of these substances increased in the presence of these vapours[8]. The solute, here the vapour, is most likely dispersed along the crystal defects and glide planes in the crystal. The mere introduction of a foreign molecule into a perfect lattice would distort the lattice locally and create a defect[10]. It has also been proved that water can penetrate rock salt[4]. It is likely, therefore, that the water vapours taken up by adsorption accompanied by absorption enter into the crystal lattice and create

defects *in* the lattice. The water molecules which penetrate into the lattice weaken the binding forces due to its fairly large magnitude of the dielectric constant ; as a result the electrons inside the lattice become more mobile. These mobile electrons pass much easily to the conduction level and the conductivity of the crystal increases.

It is evident from Fig. 1 that the conductance increases with increase of the relative humidity. It has been shown by Warburg[11] that an application of an electromotive force can bring about diffusion in an ionic crystal. The increased adsorption of moisture at higher relative humidities is thus facilitated by the applied potential through increased diffusion and hence results in an increase of current.

Thus it is possible that an adsorption mechanism is operative and the water molecules which enter the crystals alter the mobility of the electrons and bring them to the conduction level. The water molecules also increase the ionization resulting in an increase in the conductance of the crystal. As the atmosphere surrounding the crystals becomes richer in water vapour, the amount of water vapour absorbed increases and hence there will be a rapid change in the conductance at higher relative humidities.

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Synthesis of 6-Substituted Azo-5,7-Dimethyl (or Diphenyl) 2,3-Dihydro-6H-1,4-Diazepines

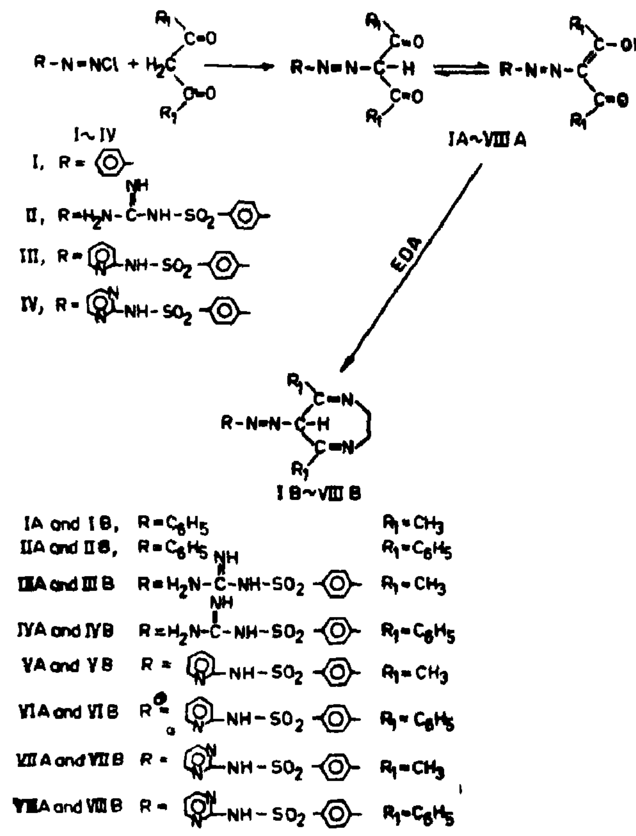
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Diazonium salts of aniline and substituted sulphanilamides were reacted with 2, 4-pentadione and dibenzoylmethane. The intermediates were identified as 3-substituted azo-2,4-pentadiones (IA, IIIA, VA and VIIA) and substituted azo dibenzoylmethane (IIA, IVA, VIA and VIIIA). On reacting IA-VIIIA with 1, 2-diaminoethane 6-substituted azo-5,7-dimethyl (or diphenyl)-2,3-dihydro-6H-1,4-diazepines (IB-VIIIB) were obtained. The structures to IA-VIIIA and IB-VIIIB were assigned on the basis of elemental analyses and spectral studies.

DIAZEPINES and its related compounds are potent CNS drugs used as tranquiliser, muscle relaxant psychosedative anticonvulsant, etc.[1-4]. The present work deals with the syntheses of a new class of compounds in which various substituted azo compounds were attached to 1,4-diazepine moiety at position 6 in order to combine the bacterostatic[5] and CNS activity in a single molecule. For this purpose, a start was made by diazotising aniline and substituted sulphanilamides separately and condensing diazonium salts with the diketones (viz. 2, 4-pentadione and dibenzoylmethane). After having established the structures, the azo compounds (IA-VIIIA) were refluxed for 8-10 hr. with 1, 2-diaminoethane in absolute ethanol. The reaction mixtures were kept in freeze overnight when solid separated out. Repeated crystallisation resulted in pure sample of the corresponding diazepine derivatives(IB-VIIIB).



Experimental

All the melting points are uncorrected. Ir spectra were recorded on a Perkin-Elmer Infracord, Nmr spectra were recorded on a Varian A-60D model using TMS as internal reference.

3-(Guanidylsulphonamidobenzeneazo)-2,4-Pentadione (IIIA)

To an ice cold solution of acetylacetone (1.0 g., 0.01*M*) in acetone containing anhy. CH_3COONa (60.0 g) a diazotised solution of sulphaguanidine (2.14 g., 0.01*M*; diazotized with dil HCl and $NaNO_2$ at 0-5°) was gradually added at 0-5° with constant stirring. The stirring was further continued for 15 min and the azo compound was precipitated by the addition of cold H_2O. The precipitated solid was filtered, washed with H_2O and dried. The crude product was crystallised from glacial CH_3COOH (IIIA, m.p. 258°; yield 2.14 g., 65.87%).

Analysis

Found : C, 44.08 ; H, 4.49 ; N. 21.78%

Calcd. for : $C_{12}H_{15}O_4N_5S$ C, 44.31 ; H, 4.62 ; N, 21.54%.

6-(Guanidylsulphonamidobenzeneazo)-5, 7-Dimethyl-2, 3-Dihydro 6H-1, 4-Diazepine (IIIB)

To IIIA (1.6250 g., 0.005*M*) taken in absolute C_2H_5OH (10 ml) 1, 2-diaminoethane (1.5 g.,

Table—1

Compound Number	Molecular Formula	Melting Point	Yield %	Analysis %					
				Calculated			Found		
				C	H	N	C	H	N
IA	$C_{11}H_{12}O_2N_2$	90°	69.61	64.71	5.88	13.73	64.40	6.08	13.91
IIA	$C_{21}H_{16}O_2N_2$	150°	67.00	76.83	4.88	8.54	76.47	5.12	8.81
IIIA	$C_{13}H_{14}O_4N_6S$	258°	66.77	44.31	4.62	21.54	44.08	4.49	21.78
IVA	$C_{22}H_{18}O_4N_6S$	240°	66.82	58.80	4.23	15.59	59.12	4.40	15.88
VA	$C_{16}H_{16}O_4N_4S$	235°	69.44	53.33	4.44	15.55	53.10	4.72	15.25
VIA	$C_{26}H_{20}O_4N_4S$	230°	64.88	64.46	4.13	11.57	64.26	4.32	11.75
VIIA	$C_{15}H_{15}O_4N_5S$	210°	66.48	49.86	4.16	19.39	49.58	4.32	19.62
VIIIA	$C_{25}H_{19}O_4N_5S$	221°	64.33	61.86	3.91	14.43	62.10	3.68	14.84

Table—2

Compound Number	Molecular Formula	Melting Point	Yield %	Analysis %					
				Calculated			Found		
				C	H	N	C	H	N
IB	$C_{13}H_{16}N_4$	185°	64.91	68.42	7.02	24.56	68.68	6.80	24.28
IIB	$C_{23}H_{20}N_4$	205°	59.66	78.41	5.68	15.91	78.71	5.43	15.72
IIIB	$C_{14}H_{19}O_2N_7S$	295°	63.04	48.14	5.44	28.08	48.48	5.24	27.80
IVB	$C_{24}H_{22}O_2N_7S$	301°	61.31	60.89	4.86	20.72	61.17	4.68	20.46
VB	$C_{19}H_{20}O_2N_6S$	305°	63.80	56.25	5.21	21.88	55.94	5.89	22.12
VIB	$C_{29}H_{24}O_2N_6S$	290°	61.02	66.14	4.72	16.54	65.86	4.93	16.52
VIIB	$C_{17}H_{19}O_2N_7S$	248°	62.34	52.99	4.94	24.45	52.69	5.15	25.66
VIIIB	$C_{27}H_{23}O_2N_7S$	261°	59.92	63.65	4.52	19.25	63.32	4.72	19.47

0.025*M*) was added with shaking and cooling. The contents were refluxed for 8 hr. and cooled to room temperature. The reaction mixture was kept in freeze overnight when orange coloured solid settled. The crude product was crystallised from C_2H_5OH (IIIB, m.p. 295°, yield 1.10 g., 63.04%).

Analysis

Found : C, 48.48 ; H, 5.24 ; N, 27.80%

Calcd. for : $C_{14}H_{19}O_2N_7S$
C, 48.14 : H, 5.44 ; N, 28.08%

Similarly IB, IIB, IVB-VIIIB were prepared. The melting points, yields and elemental analyses of these compounds are compiled in Table 2.

Structural Elucidation

Compound IA-VIIIA : On the basis of elemental analyses the molecular formulae to IA-VIIIA were suggested as shown in Table 1.

In the Ir spectra[1] of IA-VIIIA, the presence of carbonyl group was established on the basis of characteristic peaks at 1670-1650 cm^{-1} and 1265-1260 cm^{-1}. In the Ir spectra of IA-VIIIA the characteristic absorption bands at 1570 cm^{-1}, 1406±4 cm^{-1} were assigned to N=N group in these molecules. The presence of sulphonamide group in IIIA-VIIIA was established by the characteristic band in the vicinity of 1330 cm^{-1}.

In the Nmr spectra studies (c.f. Table 3) the presence of six protons for two methyl groups in IA,

Table—3

(Nmr spectra – Chemical shifts expressed in δ ppm)

Compound Number	NH-protons δ(DMSO)	Aromatic protons	$-C-CH_3$-protons
IA	–	7.0-7.7 / 5H	2.4(d) / 6H
IIA	–	6.6-7.8 / 15H	–
IIIA	9.2(b) / 4H	6.7-8.2 / 4H	2.4-2.5(d) / 6H
IVA	9.2(b) / 4H	6.7-8.2 / 14H	–
VA	9.1-9.8(b) / 1H	6.7-8.2 / 8H	2.4-2.5(d) / 6H
VIA	9.1-9.8(b) / 1H	6.7-8.2 / 18H	–
VIIA	9.1-9.3(b) / 1H	6.7-8.2 / 7H	2.4-2.5(d) / 6H
VIIIA	9.1-9.8(b) / 1H	6.7-8.2 / 17H	–

b=broad ; d=doublet.

IIIA, VA and VIIA were established on the basis of the signal as doublet in the region δ2.4-δ2.5. The signals as complicated pattern for the aromatic protons in the Nmr of IA-VIIIA were observed in the range of δ6.6-δ8.2. The signal for the proton as –CH was, however, not found in any of these Nmr spectra, indicating thereby the existence of these compounds in enolic form in acidic medium. The presence of four protons attached to nitrogens in

IIIA with and IVA were established on the basis of a broad signal in the vicinity of δ9.2 while the signal for one proton attached to nitrogen in VA-VIIIA was also found in the range of δ9.1-δ9.3

On the basis of these observations the structures the IA-VIIIA were assigned as :

3-(Phenylazo)-2,4-pentadione to IA, (Phenylazo)-dibenzoylmethane to IIA, 3-(guanidylsulphonamido-benzeneazo)-2,4-pentadione to IIIA, (guanidylsulphonamidobenzeneazo)dibenzoylmethane to IVA, 3-(pyridylsulphonamidobenzeneazo)-2,4-pentadione to VA, (pyridylsulphonamidobenzeneazo)dibenzoylmethane to VIA, 3-(pyrimidylsulphonamidobenzeneazo)-2,4-pentadione to VIIA and (pyrimidylsulphonamidobenzeneazo)dibenzoylmethane to VIIIA.

Compound IB-VIIIB

On the basis of elemental analyses the molecular formulae to IB-VIIIB were suggested as shown in Table 2.

Comparison of the Ir spectra of IB-VIIIB with that of the corresponding azo derivatives of diketones (IA-VIIIB), indicated the absence of characteristic absorption bands at 1670-1650 cm^{-1} and 1265-1260 cm^{-1}, position assigned for carbonyl group in IA-VIIIA, concluding thereby that the carbonyl groups of IA-VIIIA reacted with 1,2-diaminoethane.

The Nmr spectra of IB-IIIB, VB and VIIB (c.f. Table 4) indicated the presence of the signal for six protons at δ 2.8. a broad signal for four protons in the range of δ4.1-δ4.3, a signal as a bump for a proton in the range of δ3.3-δ3.7 and the signals as a complicated pattern for aromatic protons in the range of δ6.6-δ8.4. The signal for proton attached to nitrogen was observed in the range of δ9.2-δ9.9. in the Nmr spectra of IIIB, VB and VIIB. In the Nmr spectra of IIB, IVB, VIB and VIIIB (c. f. Table 4) indicated the presence of one methine proton in the range of δ3.5-δ3.7, four protons, i.e., two $-N-CH_2-$ groups in the region δ4.2-δ4.4 and aromatic protons in the region δ6.3-δ8.5. The proton attached to the nitrogen was found to be present in the region δ9.2-δ9.9 in the Nmr spectra of IVB, VIIB and VIIIB.

On the basis of these observations the structures to IB-VIIIB were assigned as 6-(phenylazo)-5,7-dimethyl-2,3-dihydro-6H-1,4-diazepine to IB, 6-(phenylazo)-5, 7-diphenyl-2, 3-dihydro-6H-1, 4-diazepine to IIB. 6-(guanidylsulphonamidobenzeneazo)-5, 7-dimethyl-2, 3-dihydro-6H-1,4-diazepine to IIIB, 6-(guanidylsulphonamidobenzeneazo)-5,7-diphenyl-2,3-dihydro-6H-1,4-diazepine to IVB, 6-(pyridylsulphonamidobenzeneazo)-5, 7-dimethyl-2, 3-dihydro-6H-1, 4-diazepine to VB, 6-(pyridylsulphonamidobenzeneazo)-5, 7-diphenyl-2, 3-dihydro-6H-1, 4-diazepine to VIB, 6-(pyrimidylsulphonamidobenzeneazo)-5, 7-dimethyl-2, 3-dihydro-6H-1,4-diazepine to VIIB and 6-(pyrimidylsulphonamidobenzeneazo)-5,7-diphenyl-2,3-dihydro-6H-1, 4-diazepine to VIIIB.

TABLE—4

(Nmr spectra—Chemical shifts expressed in δ ppm)

Compound number	$-NH$ protons δ(DMSO)	Aromatic protons	$=N-CH_2$ protons	CH protons	$=C-CH_3$ protons
IB	–	7.2-7.8 / 5H	4.2(b) / 4H	3.3(b) / 1H	2.8(s) / 6H
IIB	–	6.3-7.8 / 15H	4.3(b) / 4H	3.5(b) / 1H	–
IIIB	9.2-9.9 / 4H	6.6-8.4 / 4H	4.1-4.3(b) / 4H	3.3-3.7(b) / 1H	2.8(s) / 6H
IVB	9.2-9.9 / 4H	6.3-8.5 / 14H	4.2-4.4(b) / 4H	3.5-3.7(b) / 1H	–
VB	9.5-9.9 / 1H	6.6-8.4 / 8H	4.1-4.3(b) / 4H	3.3-3.7(b) / 1H	2.8(s) / 6H
VIB	9.5-9.9 / 1H	6.3-8.5 / 18H	4.2-4.4(b) / 4H	3.5-3.7(b) / 1H	–
VIIB	9.5-9.6 / 1H	6.6-8.4 / 7H	4.1-4.3(b) / 4H	3.3-3.7(b) / 1H	2.8(s) / 6H
VIIIB	9.5-9.6 / 1H	6.3-8.5 / 17H	4.2-4.4(b) / 4H	3.5-3.7(b) / 1H	–

b=broad ; s=singlet.

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Polycyclic Systems. Part XVIII.[1] Synthesis of Methyl 2-(1-Naphthyl)-5-Oxocyclopent-1-enylacetate, Methyl β-5-(1-Naphthyl)-2-Furylpropionate, and a Few Related Compounds

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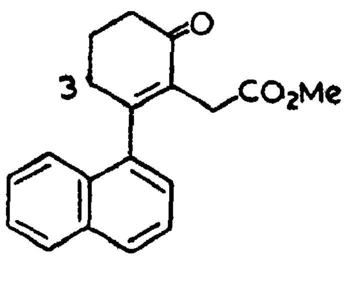
Manuscript received 9 March 1978, accepted 5 May 1978

The furfurylidene derivative of 1-acetylnaphthalene on acidic hydrolysis affords a mixture of acids which on successive treatment with alkali and methanolic hydrogen chloride yields methyl 2-(1-naphthyl)-5-oxocyclopent-1-enylacetate(III) and methyl β-5-(1-naphthyl)-2-furylpropionate(V) in 50 : 50 ratio. The formation of the furanoid compound is atypical but not unusual. The dynamic n.m.r. of the ketoester(III) indicates a low energy barrier to rotation about the aryl-cyclopentenone bond. 2-p-Methoxyphenyl-5-oxocyclopent-1-enylacetic acid(X) is likewise prepared and found to resemble closely a byproduct reported to arise from an alleged acid-induced dicyclisation of 4, 7-diketo-7-p-methoxyphenylheptanoic acid(VIII) and to which a phenalenone structure(IX) was given.

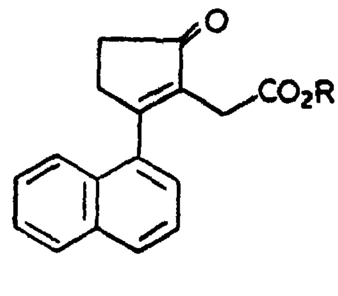
DURING our studies on restricted rotation in some arylcyclohexenone derivatives,[2,3] the highest barrier (22.B k cal mol^{-1}) was encountered in methyl 2-(1-naphthyl)-6-oxocyclohex-1-enylacetate(I) originating from a peri-interaction between 8-H of the naphthyl and 3-H of the cyclohexenyl ring. In that context, we thought that a similar study on a related cyclopentenone system (*e.q.*, III) would reveal some basic difference in the geometry of cyclohexenone and cyclopentenone moiety. *A priori*, the latter with a more or less flat ring would offer less steric resistance to any neighbouring atom or group across the pivotal bond. It is indeed found that while the coalescence temperature of the AB-quartet of the side-chain methylene protons in (I) is 183°, the same for (III) is below −90°. The synthesis of methyl 2-(1-naphthyl)-5-oxocyclopent-1-enylacetate(III) is modelled after the well-known procedure of Robinson[4] for the 2-naphthyl analogue but is not exactly typical[5-7]. This and the synthesis of a few related compounds which may hopefully resolve the structure of an allegedly unusual by-product during acid-induced athanolysis of furfurylidene *p*-methoxyacetophenone[8] form the subject matter of this communication.

1-Acetylnaphthalene was condensed with furfuraldehyde in presence of aqueous alkali to give the furfurylidene derivative which resisted all attempts to crystallise. The n.m.r. spectrum, τ(CCl_4, 100 MHz) 1.65 (1 H, d, *J* 9Hz, 8-H), 2.10-2.40 (4 H, m, 4ArH), 2.45-3.00 (5 H, m, 3ArH+2 vinylic H), 3.49 (1H, d, *J* 3.3 Hz, 3′-H), and 3.65 (1H, m, 4′-H), however, agreed well with the structure(VI). It was hydrolysed by boiling hydrochloric acid first in ethanol and then in acetic acid,[4,7] to furnish an acidic product (yield, 50%) which proved to be a 50 : 50 mixture of 4,7-diketo-7-(1-naphthyl)heptanoic acid(VII) and β-5-(1-naphthyl)-2-furylpropionic acid(IV), the integration of the two furyl protons (4-H and 3-H) at τ3.45 and 3.82 giving an accurate measure of the ratio. This appears to be the first example of a furan-derivative being formed under this condition although alcoholysis of analogous furfurylidene ketones in dry butanol[9] or ethanol[10] saturated with hydrogen chloride is known to give furanoid compounds. In the present case, ring-closure takes place in presence of water and seems to be facile due to the partial release of steric strain inherent in 1-naphthoyl system. Rate enhancement of cyclisation by steric crowding has previously been discussed[11,12]. Ring-closure of the diketo-acid(VII) was effected with dilute alkali and the combined acids were esterified to furnish methyl 2-(1-naphthyl)-5-oxocyclopent-1-enylacetate(III) and methyl β-5-(1-naphthyl)-2-furylpropionate(V) in equal amounts as determined by the two carbomethoxy peaks at τ6.50 and 6.33 respectively. The esters were separated by column chromatography and characterised by spectral data. As already stated, the methylane protons in the acetate side-chain in (III) appeared as a singlet at τ6.92 and remained so down to −90° indicating a low energy barrier to rotation.

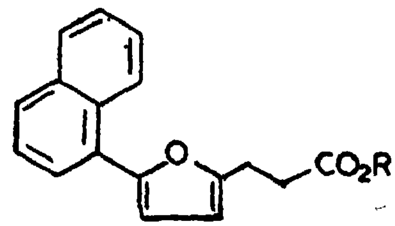
At this point, our attention was drawn to



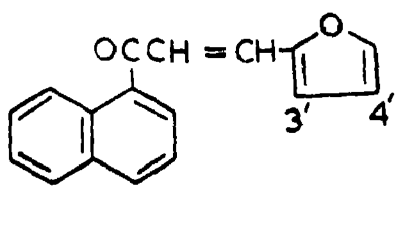
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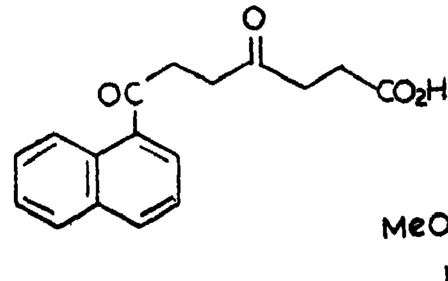
II, R=H
III, R=Me



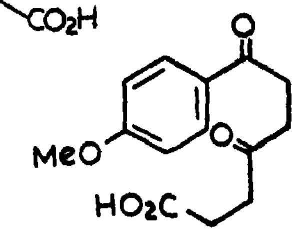
IV, R=H
V, R=Me



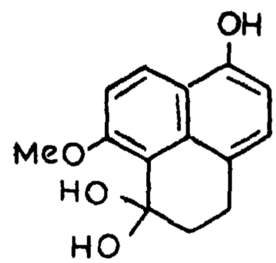
VI



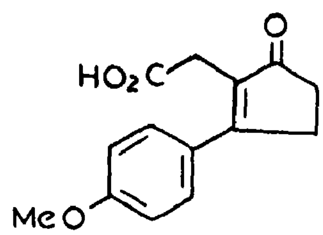
VII



VIII



IX



X

a preliminary communication by Vijayasarathi and Krishna Rao[8] in which they reported the isolation of a by-product, m.p. 95° in trace amount during acid-induced ethanolysis of furfurylidene *p*-methoxyacetophenone along with β-5-*p*-methoxyphenyl-2-furyl-propionic acid (and ester) as major product. They formulated it as 6-hydroxy-9-methoxy-2, 3-dihydrophenalen-1-one (as hydrate IX) supposed to originate from a double cyclisation of the intermediate diketo-acid(VIII). The structure was based on elemental analysis and n.m.r. of both the ketone-hydrate(IX) and the derived dinitrophenylhydrazone. A more logical proposition is an acid-catalysed aldol condensation and dehydration to 2-*p*-methoxyphenyl-5-oxocyclopent-1-enylacetic acid(X) which is a typical reaction of 1, 5-diketone leading to cyclohexenones[13,14]. A sample of 4,7-diketo-7-*p*-methoxyphenylheptanoic acid(VIII) was, therefore, prepared by acidic hydrolysis of furfurylidene *p*-methoxyacetophenone[15] and cyclised to the desired keto-acid(X) with aqueous alkali this time without encountering any furan-derivative. The acid was obtained as a monohydrate. m.p. 95° (from aqueous methanol)[16] as well as an anhydrous form, m.p. 137° (from ethyl acetate-petroleum). The latter exhibited an n.m.r. spectrum, τ($CDCl_3$, 90 MHz) 1.33 (1 H, br.s, CO_2H, exchangeable with D_2O), 2.50 (2 H, d, *J* 9Hz, 2ArH), 3.00 (2 H, d, *J* 9Hz, 2ArH), 6.15 (3H, s, OMe), 6.53 (2 H, s, CH_2CO_2H), 7.03 (2 H, m, CH_2), and 7.40 (2 H, m, CH_2) which was remarkably similar to that reported for the above-mentioned by-product[8]. The aromatic AB-quartet is very characteristic of a *p*-methoxyphenyl moiety as in (X) but rather a misfit for (IX). The m.p., however, tallied with that (95°) of our hydrated acid (as X). We were informed* that the m.p. of the by-product was taken before drying and the n.m.r. and elemental analysis were done probably with the dried sample. The dinitrophenylhydrazone of the keto-acid had m.p. 245° slightly lower than the reported one (252°) but its n.m.r. spectrum taken in trifluoroacetic acid was identical, peak by peak, to the one described for the by-product (see Experimental) with one exception that an extra methylene peak due the acetic acid side-chain in (X) was found partially buried in the methoxy peak at τ 5.90 and might have been missed by the previous workers. In all probability, therefore,

* Personal communication from Professor Krishna Rao who regretted his inability to provide us with any sample or spectrum for comparison.

the reported by-product in the ethanolysis reaction is 2-*p*-methoxyphenyl-5-oxocyclopent-1-enylacetic acid(X) although we could not be absolutely sure in absence of a direct comparison.

Experimental

All b.p.s and m.p.s are uncorrected. N.m.r. spectra were taken on 90 and 100 MHz machines for solutions in $CDCl_3$ (unless otherwise stated) with tetramethylsilane as internal standard. The low temperature n.m.r. spectra of (III) were taken on a Varian XL-100 100 MHz spectrometer in CD_2Cl_2 solution. Petroleum refers to a fraction of b.p. 40-60°. All organic extracts were dried over anhydrous sodium sulphate.

1-Acetylnaphthalene : Commercial 1-acetylnaphthalene containing 10% of 2-isomer was purified through conversion into picrate, recrystallisation, and subsequent regeneration of the ketone by passing the solution of picrate in benzene over a column of neutral alumina. 1-Acetylnaphthalene thus obtained was found to be pure by g.l.c.

Furfurylidene 1-Acetylnaphthalene (*VI*) : Ethanolic sodium hydroxide (0.8%, 2 ml) was added to a solution of 1-acetylnaphthalene (20.0 g) and freshly distilled furfuraldehyde (10.0 g) in ethanol (70 ml). After 20 hr. at room temperature, a heavy gum settled down, the mother liquor was decanted off, the residual gum taken up in methanol (30 ml), cooled to 0°, and the supernatant mother liquor again decanted off. The process was repeated a second time, the orange gum taken up in ether, the ethereal solution washed successively with dilute hydrochloric acid and water, dried, and solvent evaporated to furnish the *furfurylidene derivative* (*VI*) as a red viscous oil (11.2 g) ; ν_{max} ($CHCl_3$) 1665, 1625, 1602, and 1554 cm^{-1}. All attempts to crystallise failed and this crude product was used in the next operation.

Hydrolysis of the Furfurylidene Derivative (*VI*) : A mixture of the foregoing furfurylidene derivative (11.0 g), concentrated hydrochloric acid (12.0 ml), and ethanol (40.0 ml) was refluxed for 14 hr. Ethanol was removed at the water pump and the residue was boiled with a mixture of concentrated hydrochloric acid (12.0 ml), water (55.0 ml), and acetic acid (55.0 ml) for 2-3 hrs. The hot solution was filtered through glass wool and the filtrate was cooled to afford a dark heavy oil. The mother liquor was decanted on to the original black gum and the process was repeated several times [7]. At the end, the combined organic material (6.7 g) was dissolved in aqueous sodium hydrogen carbonate, neutral material removed by extraction with ether, and the solution acidified to give a mixture of the acids(IV) and (VII) which was taken up in methylene dichloride. Evaporation of the solvent furnished a gum (5.5 g) which proved to be a 50 : 50 mixture of the above two acids ; ν_{max}($CHCl_3$) 1715, 1688 ; ν_{max} ($CHCl_3+Et_3N$) 1710, 1685, and 1600 cm^{-1} ; τ(100 MHz)-0.60 (1 H, s, CO_2H), 1.60 (1 H, m, ArH), 2.10-2.60 (6 H, m, 6ArH), 3.45 (d, *J* 3.3 Hz, 4'-H), 3.82 (d, *J* 3.3 Hz, 3'-H) (the last two peaks integrated for 1 H), and 6.6-7.50 (6 H, m, $3CH_2$).

The above mixture (5.2 g) was taken up in aqueous 2% potassium hydroxide solution (500 ml) and heated in the water-bath for 1½ hr. The product was worked up in the usual way to afford a gum (4.7 g) which proved to be a 50 : 50 mixture of the acid(II) and (IV) by n.m.r. ; τ(100 MHz)-0.47 (s, CO_2H), 1.65 (m, ArH), 2.00-2.82 (m, ArH), 3.42 (d, *J* 3.3 Hz), 3.82 (d, *J* 3.3 Hz), 6.89 (s, CH_2-CO_2H), 6.98 (m, CH_2), 7-15-7.38 (m, CH_2) (because of the mixed nature, the proton count was not integral). The mixture of the acids (4.6 g) was esterified by refluxing methanolic 5% hydrogen chloride (80.0 ml) for 10 hr. and the esters distilled to yield an oil (4.4 g), b.p. 180-210°/0.3 mm ; n.m.r. showed it to be a 50 : 50 mixture of the esters(III) and (V) and t.l.c. (silica gel, 60 : 40 petroleum-ethyl acetate) showed two distinct spots with R_f values 0.4 and 0.6 respectively. They were cleanly separated by chromatography on a silica gel column. The ester(V) (2.0 g) was eluted with 20 : 80 ether-petroleum while the ester(III) (2.0 g) with 95 : 5 ether-petroleum.

Methyl 2-(1-Naphthyl)-5-oxocyclopent-1-enylacetate (*III*) : Methyl 2-(1-naphthyl)-5-oxocyclopent-1-enylacetate(III) was obtained in the previous experiment as a colourless viscous oil, b.p. 200-205°/0.3 mm (Found : C, 76.9 ; H, 5.9 ; M^+, 280. Calc. for $C_{18}H_{16}O_3$; C, 77.2 ; H, 5.7% ; M^+, 280) ; ν_{max} ($CHCl_3$) 1740, 1708, 1650, and 1598 cm^{-1} ; λ_{max} (EtOH) 293 nm (log ϵ4.1) (λ_{max} for I, 282 nm, log ϵ4.0) ; τ(90 MHz) 2.10 (2 H, 2d, *J* 2 and 9 Hz, 2ArH), 2.20-2.75 (5 H, m, 5ArH), 6.50 (3 H, s, CO_2Me), 6.92 (2 H, s, CH_2CO_2Me), 6.96 (2 H, t, *J* 7 Hz, 3-CH_2), and 7.30 (2 H, t, *J* 7 Hz, 4-CH_2). The *dinitrophenylhydrazone* readily formed from benzene-methanol in red needles, m.p. 196° (Found : C, 62.35 ; H, 4.7 ; N, 12.2. Calc. for $C_{24}H_{20}N_4O_6$; C, 62.6 ; H, 4.35 ; N, 12.2%) ; τ(90 MHz)-1.02 (1 H, s, NH), 0.88 (1 H, d, *J* 1.5 Hz, ArH between two NO_2), 1.70 (1 H, 2d, *J* 1.5 and 9 Hz, ArH ortho to NO_2), 2.00-2.30 (4 H, m, 4 ArH), 2.35-2.70 (4 H, m 4 ArH), 6.41 (3 H, s, CO_2Me), 6.75 (2 H, s, CH_2CO_2Me), 6.85 (2 H, t, *J* 7 Hz, 3-H_2), and 7.00 (2 H, t, *J* 7 Hz, 4-H_2).

Methyl β-5-(1-Naphthyl)-2-furylpropionate (*V*) : Methyl β-5-(1-naphthyl)-2-furylpropionate(V) was obtained as a colourless oil, b.p. 180°/0.3 mm (Found : C, 76.8 ; H, 5.8 ; M^+, 280. Calc. for $C_{18}H_{16}O_3$; C, 77.2 ; H, 5.7% ; M^+, 280) ; ν_{max} ($CHCl_3$) 1735 and 1595 cm^{-1} ; τ(90 M Hz) 1.61 (1 H, 2d, *J* 2 and 9 Hz, 8-H), 2.10-2.40 (3 H, m, 3ArH), 2.45-2.65 (3 H, m, 3ArH), 3.42 (1 H, d, *J* 3.3 Hz, 4-H), 3.82 (1 H, d, *J* 3.3 Hz, 3-H), 6.33 (3 H, s, CO_2Me), 6.90 (2 H, t, *J* 7 Hz, CH_2), and 7.28 (2 H, t, *J* 7 Hz, CH_2).

2-(p-Methoxyphenyl)-5-oxocyclopent-1-enylacetic Acid (X) : 4.7-Diketo-7-*p*-methoxyphenylheptanoic acid(VIII) prepared by acidic hydrolysis of the furfurylidene derivative of *p*-methoxyacetophenone was cyclised with aqueous 2% potassium hydroxide at 100° for 1 hr. The alkaline solution on acidification furnished a crystalline product (0.90 g) which was crystallised from aqueous methanol in colourless plates, m.p. 95° (Found : C, 63.8 ; H, 6.25. Calc. for $C_{14}H_{14}O_4$. H_2O ; C, 63.6 ; H, 6.1%) ; ν_{max}(Nujol) 3450, 1700, and 1675 cm^{-1} ; λ_{max}(EtOH) 226 and 300 nm, log ϵ 3.98 and 4.31 respectively ; τ(60M Hz) 2.35 (2 H, d, *J* 9 Hz, 2ArH), 2.85 (2 H, d, *J* 9 Hz, 2ArH). 5.10 (3 H, br. s, 3×OH, exchangeable with D_2O), 6.15 (3 H, s, OMe), 6.52 (2 H, s, CH_2CO_2H), 7.00 (2 H, m, CH_2), and 7.30 (2 H, m, CH_2). It afforded a red *dinitrophenylhydrazone*, m.p. 245° (Found : C, 56.5 ; H, 4.5 ; N, 13.0. Calc. for $C_{20}H_{18}O_7N_4$; C, 56.3 ; H, 4.2 ; and N, 13.1%) ; $\tau(CF_3CO_2H)$-0.5 (1 H, s, CO_2H), 0.70 (1 H, d, *J* 1.5 Hz, ArH), 1.37 (1 H, 2d, *J* 2 and 9 Hz, ArH), 2.20 (2 H, 2d, *J* 2 and 8 Hz, 2ArH), 2.40 (1 H, d, *J* 9 Hz, ArH), 2.70 (2 H, d, *J* 8 Hz, 2ArH), 5.85 (2 H, s, CH_2CO_2H), 5.90 (3 H, s, OMe), and 6.40 (4 H, br. s, $2CH_2$).

The above hydrated acid(X) was recrystallised from ethyl acetate-petroleum in colourless plates, m.p. 137° (Found : C, 67.3 ; H, 5.7. Calc. for $C_{14}H_{14}O_4$; C, 68.2 ; H, 5.7%) ; ν_{max}(Nujol) 1700 (sh) and 1680 cm^{-1} (reported for IX ; 1680 cm^{-1}) ; $\nu_{max}(CHCl_3+Et_3N)$ 1680 cm^{-1} and 1600 cm^{-1} ; λ_{max}(EtOH) 226 and 300 nm, log ϵ 4.06 and 4.43 respectively. The n.m.r. has already been discussed. The dinitrophenylhydrazone (red) had m.p. 245°.

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Syntheses of Some Benzofuroylcoumaran-3-Ones

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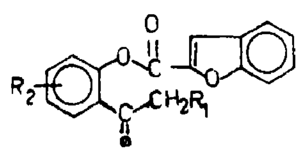
Preparation of several 2-benzofuroylcoumaran-3-ones $III_{(a-f)}$ by Baker-Venkataraman transformation of 2-(2′-benzofuroxy) ω-bromoacetophenones $II_{(a-f)}$ have been described. The ω-bromocompounds have been obtained by bromination of the corresponding acetophenones with copper(II) bromide in dry dioxan. The same coumaran-3-ones have been prepared by the cyclisation of ω-benzofuroyl-ω-bromo-2-hydroxyacetophenones $IV_{(a-f)}$ obtainable by direct bromination of the corresponding diketones with bromine in dry chloroform at 0° in the presence of potassium carbonate.

LITERATURE describing the synthesis of 2-acylcoumaranones[1-11] is not large, although such compounds have obvious possibilities in view of the biological activities[9] reported with this class of compounds. Indeed, to be best of our knowledge not a single instance is known where the acyl unit was obtained from an acid containing a heterocyclic ring system.

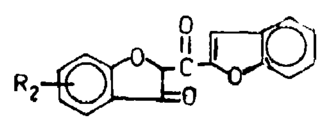
We report here the preparation of a few 2-benzofuroylcoumaran-3-ones.

The bromo intermediates $V_{(a-f)}$ under the experimental conditions will necessarily be unstable and suffer ready cyclisation to $III_{(a-f)}$.

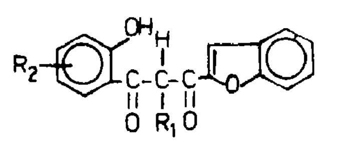
Alternatively the 1 : 3 diketones $IV_{(a-f)}$[13] were subjected to bromination in dry chloroform at 0° in the presence of anhydrous potassium carbonate by bromine in chloroform adopting a suitable modification of the method of Geissman and Armen[6]. The bromo compounds. however, could not be obtained in pure state as repeated crystallisation did



$I_{(a-f)}$



$III_{(a-f)}$



$IV_{(a-f)}$

	R_1	R_2		R_2		R_1	R_2
I_a	H	H	III_a	H	IV_a	H	H
I_b	H	5-CH_3	III_b	5-CH_3	IV_b	H	5-CH_3
I_c	H	5-Cl	III_c	5-Cl	IV_c	H	5-Cl
I_d	H	5-Br	III_d	5-Br	IV_d	H	5-Br
I_e	H	4-CH_3	III_e	6-CH_3	IV_e	H	4-CH_3
I_f	H	3 CH_3	III_f	7-CH_3	IV_f	H	3-CH_3

$II_{(a-f)} = I_{(a-f)}$, where R_1 = Br ; $V_{(a-f)} = IV_{(a-f)}$, where R_1 = Br.

The esters $I_{(a-f)}$[13] were first brominated to the w-bromoesters by means of cupric bromide in anhydrous dioxan, a reagent which selectively brominates a side chain[10,11]. In the majority of the cases the brominated products were produced in excellent yield. On subjecting the w-bromoesters $II_{(a-f)}$ to Baker-Venkataraman transformation by potassium hydroxide in dry dioxan, the desired 2-benzofuroylcoumaran-3-ones $III_{(a-f)}$ were directly obtained, obviously through the intermediates $V_{(a-f)}$, which were not isolated. The formation of the postulated intermediates find support from the works of Wheeler *et al*[8,12] in connection with the mechanism of Baker-Venkataraman rearrangement.

not improve the melting point apparently indicating some degree of cyclisation during recrystallisation. The chloroform solutions containing the bromo compounds were, therefore, directly refluxed to produce the corresponding coumaran-3-ones $III_{(a-f)}$. The yields, however, were not as good as obtainable by the first method.

All the coumaran-3-ones obtained by two methods were identical and 11 gave positive ferric reaction. Their elemental analysis and *i.r.* data agreed well with expected values. (OH at 3420-50 cm^{-1}, and 1 : 3 diketone group at 1540-1640 cm^{-1})[14].

Experimental

Melting points, determined in open capillaries are uncorrected. The i.r. spectra were recorded in Beckman infrared spectrometer Model DK-2A.

2-(2'-Benzofuroxy)-w-bromo acetophenones :— Finely powdered copper(II) bromide (0.02 mole) was added to anhydrous dioxan (60 ml) and refluxed for 30 min with exclusion of moisture. After cooling the 2-(2'-benzofuroxy) acetophenone (0.01 mole) was added to the mixture and refluxing was continued for 2½ hrs. A grey white precipitate collected at the bottom of the flask showing the formation of copper(I) bromide. After cooling copper(I) bromide was filtered off at the pump. Dioxan was partially removed under reduced pressure, and the filtrate was diluted with water. The products when viscous were extracted with benzene, washed and dried ($MgSO_4$). The residue left after removal of the solvent was recrystallized from suitable solvent. The names, yields, colours, m.ps. and solvents of recrystallisation are given below :

IIa. *2-(2'-Benzofuroxy-ω-bromoacetophenone*, 81%, m.p. 128-29° (Methanol). (Found : C., 56.5 ; H, 3.0 ; $C_{17}H_{11}O_4Br$ requires C, 56.8 ; H, 3.1%).

IIb. *5-Methyl-2-(2'-benzofuroxy)-ω-bromoacetophenone*, 49%, brownish yellow, m.p. 135-36° (Ethanol), (Found : C, 57.6 ; H, 3.4 ; $C_{18}H_{13}O_4Br$ requires C, 57.9 ; H, 3.5%).

IIc. *5-Chloro-2-(2'-benzofuroxy)-ω-bromoacetophenone*, 80%, light yellow, m.p. 145-46° (Ethanol). (Found : C, 51.4 ; H, 2.6 ; $C_{17}H_{10}O_4BrCl$ requires C, 51.8 ; H, 2.5%).

IId. *5-Bromo-2-(2'-benzofuroxy)-ω-bromoacetophenone*, 80%, light brown, m.p. 139-41°, (Ethanol) (Found : C, 46.4 ; H, 2.0 ; $C_{17}H_{10}O_4Br_2$ requires C, 46.6 ; H, 2.3%)

IIe. *4-Methyl-2-(2'-benzofuroxy)-ω-bromoacetophenone*, 33%, brownish yellow, m.p. 121-22° (Ethanol). (Found : C, 58.2, H. 3.3 ; $C_{18}H_{13}O_4Br$ requires C, 57.9 ; 3.5%).

IIf. *3-Methyl-2-(2'-benzofuroxy)-ω-bromoacetophenone*, gummy mass.

Coumaran-3-ones III $_{(a-f)}$:

First Method (General Procedure)

The mixture of a w-bromoacetophenone, II $_{(a-f)}$, anhydrous dioxan (20 ml) and potassium hydroxide (a little more than one mole per mole of ester) was gently refluxed for ½ hr. A yellow solid separated during heating. It was then cooled and treated with excess of dilute sulphuric acid. The solid which separated was filtered, washed, dried and recrystallised from ethanol. The names, yields, colours and m.ps. are given below :—

IIIa. *2-(2'-Benzofuroyl)coumaran-3-one*, 98%, reddish brown, m.p. 157-58°.

IIIb. *5-Methyl-2-(2'-benzofuroyl)coumaran-3-one*, 90% orange yellow, m.p. 172-73°.

IIIc. *5-Chloro-2-(2'-benzofuroyl)coumaran-3-one*, 70% yellow, m.p. 150-52°.

IIId. *5-Bromo-2-(2'-benzofuroyl)coumaran-3-one*, 90%, yellow, m.p. 174-75°.

IIIe. *6-Methyl-2-(2'-benzofuroyl)coumaran-3-one*, 83%. brownish yellow, m.p. 161-62°.

IIIf. *7-Methyl-2-(2'-benzofuroyl)coumaran-3-one*, 15% (of the acetophenone) brownish yellow, m.p. 164-65°.

Second Method (General Procedure) :—

To the solution of a 1 : 3 diketone (IV_{a-f}) in dry chloroform containing anhydrous potassium carbonate, molar proportion of bromine in dry chloroform was slowly added at 0° with stirring, till the colour due to bromine disappeared. The solution was next refluxed for 1 hr. cooled and filtered. The solid was boiled with water and the hot filtrate on cooling and acidification deposited crystals of the coumaran-3-one which were collected and recrystallised.

Repeated extraction of the chloroform filtrate with sodium carbonate (5%) and acidification of the alkaline extract gave an additional amount of the product although in small amounts.

The yields calculated on the basis of the diketone taken are given below :

IIIa	33.5%	IIIb	15.5%	IIIc	23.5%
IIId	61%	IIIe	37%	IIIf	20%

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Thiazole Derivatives : N-Substituted Phthalimides

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A series of N-substituted phthalimides containing thiazole, benzothiazole and naphthothiazole nuclei have been synthesised. All the compounds have been screened for their fungicidal activity. Some of them have also been tested for their antispasmodic and antihistaminic activities.

N-substituted phthalimides have been reported to exhibit antifungal[1-3], antibacterial[3-5], antitumor[6-8], anthelmintic[9], local anesthetic[10], diuretic[11], adrenolytic[12] and schistosomicidal[13] properties. Compounds containing thiazole and benzothiazole nuclei are well known as biologically active compounds[14-17]. In view of the above findings, the present series of compounds have been synthesised to study their biological activities.

They have been prepared by condensing N-hydroxymethyl phthalimide with 2-amino-4-substituted thiazoles, 2-amino-4-substituted benzothiazoles, 2-amino-6-substituted benzothiazoles and 2-amino naphthothiazoles. The yield of the final products are in between 60-70%. Satisfactory I.R. data and analysis (S and N) have been obtained for all the compounds.

Experimental

Melting points were determined in open capillary tubes and are not corrected.

Substituted thiazoles, benzothiazoles and naphthothiazoles

4-Aryl-2-amino thiazoles were prepared by the condensation of substituted acetophenones with thiourea in presence of iodine[17-20].

2-Amino-4(2'-thienyl)thiazole was prepared from 2-acetylthiophene, thiourea and iodine[21].

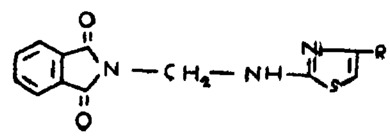
2-Amino benzothiazoles and 2-amino naphthothiazoles were prepared by the method reported by Bhargava and Baliga[22].

N-(N-Phthalimido methyl)-4-Phenyl-2-aminothiazole

N-Hydroxymethyl phthalimide (1.6 g) prepared according to known method[23] was dissolved in minimum amount of ethanol (20 ml.). To it 2-amino-4-phenyl thiazole (1.76 g) was added and refluxed for 3 hr. The reaction mixture was filtered and the filtrate was cooled sufficiently. The solid formed was filtered and recrystallised from alcohol, m.p. 220(d)°, yield – 60% (Found, S, 9.41 ; N, 12.32 ; $C_{18}H_{13}N_3SO_2$ requires, S, 9.55 ; N, 12.54%).

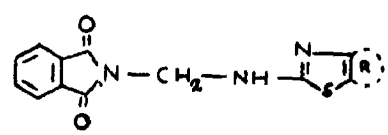
The melting points of other N-substituted phthalimides similarly prepared are given in Tables 1 and 2.

TABLE—1



Sl. No.	R	M.P. °C
1.	H	225
2.	Thienyl	170(d)
3.	Phenyl	220(d)
4.	p-Tolyl	188
5.	p-Cl-Phenyl	210(d)
6.	p-Br-Phenyl	130
7.	p-Ethoxy-Phenyl	185(d)
8.	β-Naphthyl	187

TABLE—2



Sl. No.	R	M.P. °C
9.	Phenyl	183
10.	6-Methyl-Phenyl	215
11.	6-Methoxy-Phenyl	185
12.	4-Methyl-Phenyl	225
13.	4-Cl-Phenyl	197
14.	β-Naphthyl	125
15.	α-Naphthyl	177

Fungicidal test

For fungicidal assay, poisoned food technique was used[24]. All the compounds were tested for toxicity towards *Drechslera nodulosa* fungus which

incites leaf-spot disease on ragi (*Elusine carcava*) a millet crop extensively cultivated in Orissa.

The results of the fungicidal tests indicate that presence of halogens, β-naphthyl, and methoxy group increases the fungicidal activity (Compound Nos. 5, 8, 11, 13 and 14). The percentage of germination of conidia is ~10 and ~25 at a concentration of 500 ppm and 250 ppm respectively for the above test drugs.

Antispasmodic and antihistaminic activities

Of the four compounds (Nos. 2, 3, 9 and 10) tested, the compound Nos. 9 and 10 at a concentration of 100/μg/ml completely blocked the effect of both acetylcholine chloride and histamine on the terminal ileum of guinea-pig. The return of response after washing was also slow in these cases.

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Synthesis of Sex Attractants for Cabbage Looper and False Codling Moths

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Periodic acid cleavage of epoxycyclohexane yields 1, 6-hexanedial. The sex attractants for cabbage looper and false codling moths were synthesized using a single synthetic sequence starting with 1, 6-hexanedial. The total synthesis of *cis* and *trans* 7-doceneyl acetate has been accomplished using novel synthetic techniques and the separation of isomers has been performed chromatographically. The efficiency of the synthesis is demonstrated by a 27% yield of products. The spectroscopic data obtained from the synthetic samples agree with those proposed for the attractants.

THE increasing use of insecticides and the discovery that many of these compounds are endangering man and the environment has resulted in research aimed at establishing alternate means of pest control. One of the most promising of these is the use of chemicals that influence insect chemosensory behaviour as attractants and repellents.

The sex attractant of the female cabbage looper moth *Trichoplusia ni* was isolated from virgin female cabbage looper moths and characterized as *cis*-7-dodecenyl acetate[1]. The biological activity of this attractant along with attempts of its synthesis were studied and reported in a series of papers[2-6]. The *trans* isomer of 7-dodecenyl acetate was isolated from virgin female false codling moths *Argoplace leucotreta* and synthesized separately by Berger[7] and Warren[8].

The sex pheromones for cabbage looper and false codling moths are geometrical isomers. The sequence of reactions employed for the total synthesis of these sex attractants is represented in Figure 1. Despite the low product yields, a significant feature of this approach is the synthesis of two physiologically active hormones from readily available starting materials, using a single synthetic sequence.

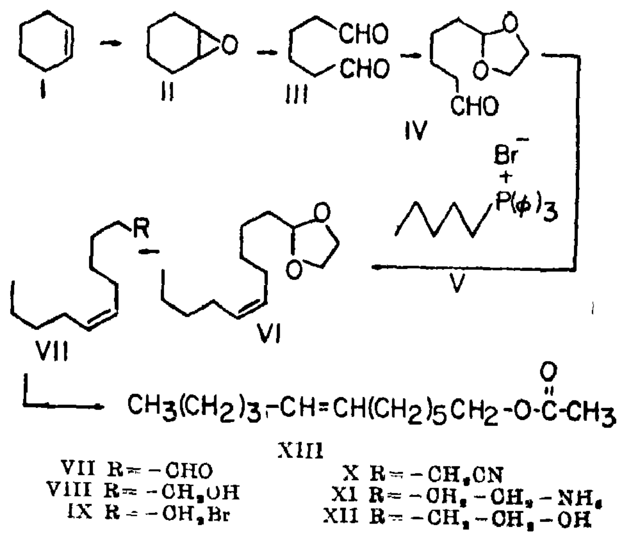


Fig. 1. Reaction Sequence for the Synthesis of 7-dodecenyl acetate.

Starting with cyclohexene the sex attractants for the cabbage looper and false codling moths were synthesized in 27% overall yield. Cyclohexene(I) was converted to its epoxide with peroxyacetic acid. Epoxycyclohexane(II) was cleaved with periodic acid to yield 1, 6-hexanedial(III)[9]. One of the aldehyde functions on (III) was blocked with ethylene glycol to yield 6-ethylenedioxy-1-hexanal (IV). The monoketal(IV) was condensed with the triphenylphosphonium salt of *n*-bromopentane (V). The resulting compound, 11-ethylenedioxy-5-undecene(VI) was hydrolyzed with dilute hydrochloric acid to 6-undecene-1-al(VII). The aldehyde function on (VII) was reduced with sodium borohydride to yield 6-undecene-1-ol(VIII). The alcohol(VIII) was subsequently converted to 5-undecenyl bromide(IX) with phosphorus tribromide. The bromoalkene(IX) on treatment with potassium cyanide gave 1-cyano-6-undecene(X). The nitrile (X) on reduction with sodium borohydride and cobalt chloride gave 1-amino-7-dodecene(XI). When deaminated with sodium nitrite at −5°, (XI) gave 7-dodecene-1-ol(XII). The alcohol (XII) upon esterification with acetyl chloride gave a mixture of *cis* and *trans*-7-dodecenyl acetate(XIII). The separation of the *cis* and *trans* isomers was effected chromatographically using a silica gel column impregnated with silver nitrate.

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The synthetic *trans*-7-dodecenyl acetate showed IR maxima at 1730 and 1040 cm^{-1} characteristic of a primary acetate group. It also showed a sharp band at 980 cm^{-1} characteristic of the C–H out of plane deformation of the *trans* disubstituted double bond. The peak at 970 cm^{-1} in the infrared spectrum of the *cis*-7-dodecenyl acetate was absent.

The mass spectral data for 7-dodecenyl acetate showed a strong parent peak at 226 m/e. The (p+1) peak was observed distinctly. The characteristic fragmentation peaks shown by acetyl esters was observed at 43 and 60 m/e. A strong peak at 70 m/e was observed, accounting for the ion formed by the breaking of the ethylenic linkage at carbon seven. The mass spectrum data is consistent with the proposed structure of 7-dodecenyl acetate.

In preliminary screening tests, the cabbage looper and the false codling moth hormones synthesized were used as bait in field trapping experiments. *Cis*-7-dodecenyl acetate caught two male cabbage looper moths over a 14-day period. Naturally-occurring lures were not used as a standard for comparison. Extensive work remains to be done in the area of screening techniques to standardize a systematic procedure to screen samples for activity. At the present time the data obtained from the preliminary screenings are inconclusive and do not provide definite results regarding the physiological activity of the hormones synthesized.

Experimental

Spectra were obtained using a Varian A-60D analytical NMR spectrometer. The samples were run both as neat liquid and in deuterated organic solvents, at ambient magnetic temperature, 39°. A filter band width of 4 Hz, a RF field of 0.015 to 0.1 mG, a sweep time of 250 sec., and a sweep width of 500 Hz were used. All spectral data obtained are reported in (δ) values with respect to tetramethyl silane peak. The IR spectra were obtained as thin films between sodium chloride plates in the region of 4000 cm^{-1} to 600 cm^{-1} using a Perkin-Elmer Model 700 spectrophotometer. Molecular weights were determined using a DuPont Model 21-490, 90° single focusing mass spectrometer. Cyclohexene, obtained from Eastman Kodak Chemical Company, was used without further purification. Periodic acid, obtained from Matheson Chemical Company, Inc., was used without further purification. Peroxyacetic acid, 40%, in acetic acid was prepared using the procedure reported in the literature[10]. All other chemicals and solvents used were reagent grade.

1, 2-epoxycyclohexane(II) : Peroxyacetic acid, 40%, (70 g, 0.5 m) dissolved in acetic acid (80 ml) was added dropwise to a stirred, cooled (20°) solution of anhydrous sodium acetate (41.0 g, 0.5 m) and cyclohexene (41 g, 0.50 m) in chloroform (700 ml). The mixture was stirred at 50° for 2 hrs. and allowed to stir an additional 8 hrs. at room temperature. The solution was neutralized with a 1.0 *N* solution of sodium bicarbonate. The organic layer was separated, washed with water (200 ml), and dried (Na_2SO_4). The solvent was removed in vacuo and the residue was distilled to afford 43.6 g (89% yield) of (II). bp : 49° (8 mm) [Lit[11] bp : 54° (10 mm)] ; ^1H NMR ($CDCl_3$), 1.4 (t, 4H), 2.0 (m, 4H), 3.2 (t, 2H), (Found C. 73.51 ; H. 10.29 ; calc. for $C_6H_{10}O$, C. 73.46 ; H. 10.20).

1, 6-hexanedial(III) : Periodic acid (91.2 g, 0.4 m) was added in five gram portions to a stirred suspension of 1, 2-epoxycyclohexane (39.2 g, 0.4 m) in water (500 ml). As the reaction proceeded the contents were cooled with an ice bath to prevent the temperature from rising above 45°. The addition of periodic acid was completed in 3 hrs. The mixture was allowed to stir at 25° for an additional 5 hrs. The solution was neutralized with solid sodium bicarbonate to *p*H 7. The neutral solution was saturated with sodium chloride and allowed to stand at room temperature for 4 hrs. The solution was subsequently extracted with chloroform (8 × 100 ml). The combined organic fractions were washed with water (500 ml) and dried (Na_2SO_4). The solvent was removed under vacuum to afford 41.5 g of (III), as a yellow liquid. ^1H NMR (neat), 1.8 (t, 4H), 2.6 (m, 4H), 9.8 (d, 2H).

6-ethylenedioxy-1-hexanal(IV) : A solution of 1,6-hexanedial, (35.0 g, 0.3 m), ethylene glycol (18.6 g, 0.3 m), *p*-toluenesulfonic acid (100 mg), and anhydrous benzene (500 ml) was refluxed for 12 hrs. The water formed during the reaction was removed using a Dean-Stark apparatus. The solution was cooled to room temperature, filtered, washed with 0.10 *N* sodium bicarbonate, and dried ($MgSO_4$). Benzene was removed using a rotary evaporator and the residue upon distillation gave 45 g (95% yield) of (IV). bp : 118° (20 mm) ; ^1H NMR (neat), 1.6 (m, 8H), 4.0 (s, 4H), 4.9 (m, 1H), 9.8 (d, 1H).

1-pentyltriphenylphosphonium bromide (V) : A stirring mixture of *n*-bromopentane (75.5 g, 0.5 m), triphenylphosphine (131 g, 0.5 m), and toluene (200 ml) was refluxed for 8 hrs. The solution was cooled to room temperature and anhydrous ether (200 ml) was added to separate the phosphonium salt. The salt was isolated by filtration, washed with anhydrous ether and recrystallized from methanol to give 123 g (60% yield) of (V) as a white crystalline solid. Mp : 163-165° ; [Lit[12] mp 167°] ; ^1H NMR ($CDCl_3$), 0.9 (t, 3H), 1.6 (m, 6H), 3.8 (m, 2H), 7.9 (m, 15H).

11-ethylenedioxy-5-undecene (VI) : A solution of 1-pentyltriphenylphosphonium bromide (82.6 g, 0.2 ml), sodium ethoxide (13.6 g, 0.2 ml), and ethanol (300 ml) was treated dropwise with a solution of 6-ethylenedioxy-1-hexanal (31.6 g, 0.2 ml) in ethanol (100 ml). After the addition was completed, the reaction mixture was allowed to stir for

2 hrs. at 40°. The solution was cooled and allowed to stand at room temperature for 24 hrs. The solution was filtered and extracted with ether (5 × 200 ml). The combined ether extracts were washed with water (5 × 100 ml) and dried (Na_2SO_4). Evaporation of the solvent in vacuum gave 27 g of (VI) as a yellow liquid. ^1H NMR (neat), 0.8 (t, 3H), 1.5 (m, 14H), 3.8 (s, 4H), 4.8 (m, 1H), 5.8 (t, 2H).

6-undecene-1-al (VII) : A solution of 11-ethylenedioxy-5-undecene (25 g, 0.11 ml) and hydrochloric acid 0.10 *N* (100 ml) was refluxed at 95° for 4 hrs. The hot solution was poured into water (200 ml) and neutralized with 0.50 *N* sodium hydroxide. The aqueous solution was saturated with sodium chloride and extracted with chloroform (5 × 100 ml). The combined chloroform extracts were washed with water (2 × 100 ml) and dried (Na_2SO_4). The chloroform was removed under vacuum and the residue upon distillation gave 16.6 g (90% yield) of (VII). bp : 126° (10 mm) ; ^1H NMR ($CDCl_3$), 1.0 (t, 3H), 1.6 (m, 12H), 2.4 (m, 2H), 5.8 (t, 2H), 9.6 (d, 2H). (Found C. 78.73 ; H. 12.01 ; calc. for $C_{11}H_{20}O$, C. 78.57, H. 11.90).

6-undecene-1-ol (VIII) : A mixture of 6-undecene-1-ol (15.2 g, 0.9 ml), sodium borohydride (4.5 g, 0.1 ml), and ethanol (200 ml) was stirred for 4 hrs. at 40°. The reaction mixture was allowed to stir for an additional 2 hrs. at room temperature and then poured into a beaker of distilled water (500 ml). The solution was saturated with sodium chloride and extracted with chloroform (3 × 100 ml). The combined chloroform extracts were washed with water (300 ml) and dried ($MgSO_4$). The chloroform was removed in vacuum and the residue was distilled to afford 14.9 g (97% yield) of (VIII). bp : 114-116° (12 mm) ; ^1H NMR (neat), 0.9 (t, 3H), 1.6 (m, 14H), 3.8 (m, 2H), 4.8 (s, 1H), 5.7 (t, 2H). (Found C. 77.81 ; H. 13.02 ; calc. for $C_{11}H_{22}O$, C. 77.64 ; H. 12.94).

1-bromo-6-undecene (IX) : A solution of phosphorus tribromide (13.5 g, 0.050 m), lithium bromide (4.4 g, 0.050 m), in pyridine (25 ml) was added dropwise to a stirred, cooled solution of 6-undecene-1-ol (9 g, 0.050 m) in pyridine (25 ml). Throughout the addition the temperature was maintained at −30° using a slurry of acetone and liquid nitrogen. Following the addition the reaction mixture was refluxed at 80° for 2 hrs. The solution was cooled to room temperature and poured into a beaker of crushed ice. The solution was extracted with ether (3 × 100 ml). The combined ether extracts were washed with 1.0 *N* hydrochloric acid (5 × 250 ml) to separate pyridine as its hydrochloride salt. The ether layer then was washed with 1.0 *N* solution bicarbonate (2 × 200 ml), water (2 × 100 ml), and dried (Na_2SO_4). Removal of the ether under vacuum gave 111 g of (IX) in the form of a brown liquid. ^1H NMR ($CDCl_3$), 0.9 (t, 3H), 1.2-1.6 (m, 14H), 3.5 (m, 2H), 5.6 (t, 2H).

1-cyano-6-undecene (X) : A solution of sodium cyanide (4.9 g, 0.10 m), copper cyanide (8.9 g, 0.10 m), and a 1-bromo-6-undecene (10 g, 0.040 m) in dimethylformamide (50 ml) was refluxed at 90° for 16 hrs. The reaction mixture was cooled to room temperature and poured into a cold saturated solution of sodium chloride (200 ml). The solution was filtered and the aqueous solution was extracted with benzene (3 × 100 ml). The combined organic extracts were washed with water (2 × 100 ml) and dried ($MgSO_4$). The benzene was evaporated under vacuum to yield 9 g of *(X)*. ^1H NMR ($CDCl_3$), 0.9 (t, 3H), 1.6 (m, 14H), 4.0 (m, 2H), 5.6 (t, 2H).

1-amino-7-dodecene (XI) : Sodium borohydride (11.4 g, 0.30 m) was added in small portions to a stirred solution of 1-cyano-6-undecene (6.5 g, 0.036 m) and cobalt chloride hexahydrate (11.4 g, 0.3 m) in ethanol (200 ml). The temperature throughout the addition was maintained at 25° using a water bath. A black precipitate appeared during the addition of sodium borohydride. When the addition was complete, stirring was continued for 2 hrs. at 25°. Hydrochloric acid 2.0 *N* (100 ml) was poured into the reaction mixture and stirred until the black precipitate dissolved. Ethanol was removed from the solution by distillation. Any unreacted nitrile was removed from the residue by extraction with ether (2 × 100 ml). The aqueous layer was made alkaline with ammonium hydroxide. The alkaline solution was extracted with ether (3 × 100 ml). The combined ether extracts were washed with saturated sodium chloride solution (2 × 100 ml), water (1 × 100 ml), and dried (Na_2SO_4). The solvent was removed under vacuo and the residue upon distillation gave 6.0 g (92% yield) of (XI). bp : 96° (5 mm) ; ^1H NMR (neat), 1.0 (t, 3H), 1.7 (m, 12H), 3.4 (m, 6H), 5.6 (t, 2H). (Found C. 78.82 ; H. 13.61 ; N. 7.83 ; calc. for $C_{12}H_{25}N$, C. 78.68 ; H. 13.66 ; N. 7.65).

7-dodecenol (XII) : Concentrated sulfuric acid (20 ml) was added dropwise to a suspension of 1-amino-7-dodecene (6.0 g, 0.030 m) in water (100 ml). The clear solution was cooled to −3° using an ice bath. A solution of sodium nitrite (17 g, 0.25 m) in water (30 ml) was added dropwise to the cold amine solution. Following the addition of sodium nitrite the solution was allowed to stir at 0°. After 2 hrs., ice (100 g) and urea (1 g) were added to the cold solution. The solution was evaporated to 100 ml by gradual heating. The aqueous solution was cooled to room temperature and extracted with ether (2 × 100 ml). The residue was neutralized with 3.0 *N* sodium hydroxide. The neutral solution was extracted with ether (3 × 100 ml). The combined ether extracts were washed with water (2 × 200 ml) and dried (Na_2SO_4). Evaporation of the solvent gave 5.1 g of (XII) as a pale yellow liquid. ^1H NMR (neat), 1.0 (t, 3H), 1.6 (m, 16H), 3.8 (t, 2H), 4.2 (s, 1H), 5.8 (t, 2H).

7-dodecenyl acetate (XIII) : A mixture of 7-dodecenol (8.0 g, 0.05 m) and acetyl chloride (15.6 g,

0.2 m) was stirred at 45° for 11 hr. The solution was cooled to room temperature and poured into a beaker (500 ml) of crushed ice. A yellow organic layer separated to the top. The organic layer was washed with 0.10 N sodium bicarbonate solution (100 ml), water (2×100 ml), and dried ($CaCl_2$). The organic layer was distilled under reduced pressure to yield 5.5 g (90% yield) of (XIII) as a colorless liquid. bp: 78-85° (0.05 mm) [Lit[8] bp: 78-82 (0.05 mm)]; ^1H NMR (neat), 0.8 (t, 3H), 1.4 (m, 16H), 1.8 (s, 3H), 4.2 (t, 2H), 5.8 (t, 2H). (Mol. wt. found 226; calc. for $C_{14}H_{26}O_2$, 226). (Found C. 74.42; H. 11.61; calc. for $C_{14}H_{26}O_2$, C. 74.33; H. 11.50).

Separation of cis *and* trans *isomers of 7-dodecenyl acetate*: The *cis* and *trans* isomers were separated chromatographically using a column packed with silica gel impregnated with silver nitrate. The packing material for the column was prepared by drying a mixture of 20 g of silica gel and 60 ml of 15% aqueous silver nitrate in a rotary evaporator and then heating the mixture in an oven at 110° for 2 hrs. The 7-dodecenyl acetate (500 mg) was introduced on the silica gel-silver nitrate column and eluted with ether (3%) in hexane. The first fractions contained the *trans* -7-dodecenyl acetate. The latter fraction eluted with ether (10%) in hexane contained the *cis*-7-dodecenyl acetate. The *trans* isomer obtained was 340 mg (68%) and the *cis* isomer obtained was 90 mg (18%).

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Synthesis and Fungicidal Activity of Arylidene Acetoacet Hydrazides

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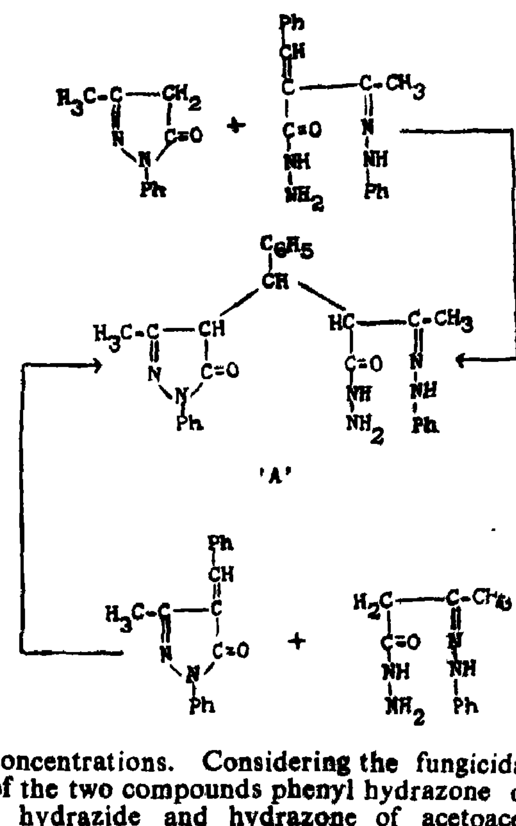
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1-Aryl-2-pyrazolin-5-ones and 4-arylidene-2-pyrazolin-5-ones on treatment with hydrazine hydrate produce respectively phenyl hydrazone of acetoacet hydrazide and arylidene derivative of above. A derivative of acetoacet hydrazide with a 5-pyrazolone ring as substituent on its active methylene carbon has been produced by two methods, both involving Michael addition of a reactive methylene derivative to a $\alpha\beta$-unsaturated carbonyl compound. 50 compounds thus prepared have been screened for their antifungal activity against the rice blast pathogen *Pyricularia orysae* and brown leaf spot pathogen *Helminthosporium orysae*.

With few exceptions, all these compounds exhibit significant antifungal activity against these two pathogens. The fungicidal activity of most of these compounds is comparable with the standard fungicides like *o*-Ethyl-S, S-diphenyl phosphorodithioate (Hinosan 50%) EC, MBC 50% WP, Difolatan 50% WP and Derosal 60% WP.

THIS is in continuation to our earlier work on heterocyclic fungicides[1-7]. It has been observed that 5-pyrazolone and its mono-arylidene derivatives[8] possess significant fungicidal activity against the rice blast pathogen *Pyricularia Oryzae* and brown leaf spot pathogen *Helminthosporium Oryzae*. When treated with hydrazine hydrate, 4-arylidene derivatives of 5-pyrazolone and the parent pyrazolone, there is ring opening and addition resulting in the formation of hydrazides. These hydrazides were found to be more active than the 4-arylidene derivatives and the parent pyrazolone itself. 24 arylidene derivatives of phenyl hydrazone of acetoacet hydrazide were prepared. The enhanced fungicidal activity of these hydrazides and the significant fungicidal activity of 5-pyrazolones encouraged us to combine both the fungicidalyactive moieties in one molecule. A derivative of acetoacet hydrazide 'A' with a 5-pyrazolone ring as substituent on its active methylene carbon has been produced by two methods both involving Michael addition of a reactive methylene derivative to a $\alpha\beta$-unsaturated carbonyl compound.



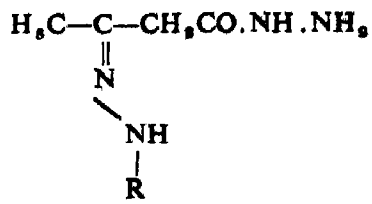
'A'

The identity of the two products obtained by two different methods was confirmed from m.m.p. and super imposition of IR absorption spectrum. 24 such addition products were prepared. It was observed that the Michael addition products displayed more fungicidal activity than the starting materials.

All the compounds prepared during the present investigation were screened for their antifungal activity against the rice blast pathogen *P. oryzae* and brown leaf spot pathogen *H. oryzae* by the standard method[9], using spore germination tests at various concentrations. Considering the fungicidal activity of the two compounds phenyl hydrazone of acetoacet hydrazide and hydrazone of acetoacet hydrazide (Sl. No. 1 and 2) (Table 1), it was observed that both these two compounds exhibit significant antifungal activity against the pathogens *P. oryzae* and *H. oryzae*.

Out of the 24 arylidene derivatives of the phenyl hydrazone of acetoacet hydrazide, it was seen that

TABLE—1



Sl. No.	Nature of 'R'	M.P. in °C	%C Found (Reqd.)	%H Found (Reqd.)	%N Found (Reqd.)	% of germination inhibition at 1000 ppm concentration.	
						P. oryzae	*H. oryzae*
1.	C_6H_5	219	58.17 (58.25)	6.81 (6.90)	27.28 (27.18)	92	80
2.	H	226	36.87 (36.90)	7.72 (7.69)	43.15 (43.15)	87	75

one compound (Sl. No. 18) (Table 2) was ineffective against the pathogen *P. oryzae* and 4 compounds (Sl. No. 18, 19, 22 and 23) did not exhibit significant activity against the pathogen *H. oryzae*. The remaining compounds showed encouraging antifungal activity against these two pathogens. Compounds (Sl. No. 6, 9 and 13) inhibited 100% spore germination of the pathogen *P. oryzae*) at 1000 ppm concentration.

In case of the 24 Michael addition products, 2 compounds (Sl. No. 42 and 45) (Table 3) did not exhibit significant antifungal activity against the pathogen *P. oryzae* and 6 compounds (Sl. No. 37, 39, 42, 44, 45 and 48) did not show antifungal activity against the pathogen *H. oryzae*. The remaining compounds showed pronounced fungicidal activity against these two pathogens. Further it was observed that compounds (Sl. No. 27, 30, 32, and 33) exhibit 100% spore germination inhibition of the pathogen *P. oryzae* at 1000 ppm concentration and compound (Sl. No. 30) inhibited 100% spore germination of the pathogen *H. oryzae* at 1000 ppm concentration. It was seen that in general the compounds showed higher germination inhibition in case of the pathogen *P. oryzae* and comparatively less inhibition against the pathogen *H. Oryzae*. The fungicidal activities of the prepared compounds were compared with standard fungicides like *o*-Ethyl-S, S-diphenyl phosphorodithioate (Hinosan 50%) EC, MBC 50% WP, Difolatan 50% WP and Derosal 60% WP which inhibited 95, 88, 98, 87% of spore germination of the pathogen *P. oryzae* at 1000 ppm concentration. It was seen that 16 compounds (Sl. No. 1, 2, 6, 8-10, 13, 15, 21, 27, 30, 31, 32, 33, 34 and 48) inhibited spore germination in the same range as the above standard fungicides and hence may be used as commercial fungicides.

Experimental

Preparation of Phenyl hydrazone of acetoacet hydrazide :

1-Ph-3-Me-2-pyrazolin-5-one (2 g) was mixed with 80% hydrazine hydrate (1.8 g). The resulting mixture was refluxed over a small flame for 4 hrs. It was then kept for overnight. A yellowish needle-shaped compound was settled at the bottom of the flask. On crystallisation from abs. alcohol, yellowish needle-shaped crystals were obtained, m.p. 219°, yield 75%. The compound is soluble in 10% sodium hydroxide and gives colouration with alcoholic ferric chloride.

Preparation of benzylidene derivative of phenyl hydrazone of acetoacet hydrazide :

1-Ph-3-Me-4-benzylidene-5-pyrazolone (2 g) was mixed with 80% hydrazine hydrate (1.5 g). The resulting mixture was refluxed over a small flame for 4 hrs. It was then kept overnight. Yellowish compound was obtained. On crystallisation from abs. alcohol, yellowish needle-shaped crystals were obtained, m.p. 162°, yield 80%. The product is insoluble in 10% sodium hydroxide and gives no colouration with alcoholic ferric chloride.

Preparation of the Michael addition product of Benzylidene derivative of phenyl hydrazone of acetoacet hydrazide and 1-Ph-3-Me-2-pyrazolin-5-one :

Method I :

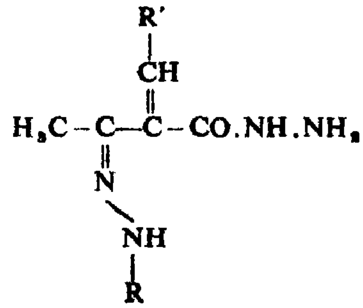
Benzylidene derivative of phenyl hydrazone of acetoacet hydrazide (1 g) was dissolved in abs. alcohol (5 ml). To it 1-Ph-3-Me-2-pyrazolin-5-one (0.6 g) dissolved in 10% sodium hydroxide (6 ml) was added, at room temperature. Immediate precipitation of a white compound occurred. On crystallisation from abs. alcohol, white needle-shaped crystals were obtained, m.p. 157°, yield 80%.

The product is soluble in 10% sodium hydroxide and gives colouration with alcoholic ferric chloride.

Method II :

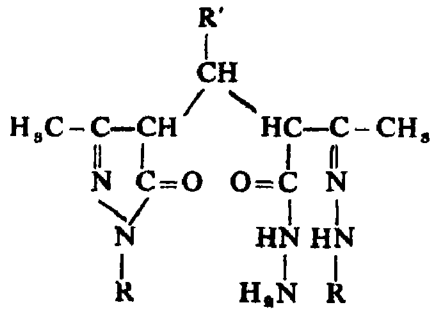
Phenyl hydrazone of acetoacet hydrazide (1 g) was dissolved in 10% sodium hydroxide (5 ml). To it 1-Ph-3-Me-4-benzylidene-5-pyrazolone (1.2 g) dissolved in abs. alcohol (5 ml) was added at room

TABLE—2



Sl. No.	Nature of R	Nature of R′	M.P. °C	%C Found (Reqd.)	%H Found (Reqd.)	%N Found (Reqd.)	% of germination inhibition at 1000 ppm conc.	
							P. oryzae	*H. oryzae*
3.	C_6H_5	C_6H_5	162	69.21 (69.38)	6.27 (6.12)	19.02 (19.04)	68	65
4.	C_6H_5	$C_6H_4NO_2$(o)	149	60.27 (60.17)	5.13 (5.01)	20.54 (20.64)	77	67
5.	C_6H_5	$C_6H_4NO_2$(m)	151	60.20 (60.17)	5.09 (5.01)	20.58 (20.64)	60	64
6.	C_6H_5	$C_6H_4NO_2$(p)	175	60.14 (60.17)	5.01 (5.01)	20.61 (20.64)	100	88
7.	C_6H_5	C_6H_4OH(o)	132	65.81 (65.80)	5.78 (5.80)	18.02 (18.06)	72	59
8.	C_6H_5	C_6H_4OH(m)	118	65.79 (65.80)	5.68 (5.80)	18.03 (18.06)	88	70
9.	C_6H_5	C_6H_4OH(p)	169	65.76 (65.80)	5.72 (5.80)	17.93 (18.06)	100	74
10.	C_6H_5	$C_6H_4CH_3O$	110	66.66 (66.66)	6.16 (6.17)	17.24 (17.28)	98	80
11.	C_6H_5	$C_6H_4N(CH_3)_2$	243	67.68 (67.65)	6.75 (6.82)	20.72 (20.77)	75	60
12.	C_6H_5	C_4H_3O	260 (d)	63.29 (63.38)	5.61 (5.63)	19.68 (19.71)	67	64
13.	C_6H_5	$C_6H_3OHCH_3O$	173	63.51 (63.52)	5.78 (5.88)	16.39 (16.47)	100	82
14.	C_6H_5	C_6H_3OHBr	127	52.41 (52.45)	4.29 (4.37)	14.32 (14.39)	62	60
15.	H	C_6H_5	221	60.54 (60.55)	6.43 (6.42)	25.59 (25.68)	92	83
16.	H	$C_6H_4NO_2$(o)	232	50.12 (50.19)	4.88 (4.94)	26.59 (26.61)	80	67
17.	H	$C_6H_4NO_2$(m)	119	50.17 (50.19)	4.86 (4.94)	26.60 (26.61)	74	60
18.	H	$C_6H_4NO_2$(p)	246	50.21 (50.19)	4.97 (4.94)	26.81 (26.61)	85	48
19.	H	C_6H_4OH(o)	91	56.42 (56.41)	5.89 (5.98)	23.87 (23.93)	60	49
20.	H	C_6H_3OHBr	308	42.20 (42.18)	4.13 (4.15)	17.78 (17.89)	80	65
21.	H	$C_6H_2CH_3OBr_2$	166	35.46 (35.48)	3.42 (3.44)	13.69 (13.79)	88	67
22.	H	$C_6H_4N(CH_3)_2$	256	59.77 (59.77)	7.27 (7.27)	26.81 (26.81)	63	49
23.	H	C_6H_4Cl	135	52.28 (52.27)	5.16 (5.14)	22.02 (22.17)	75	52
24.	H	$C_6H_4CH_3O$	164	58.13 (58.06)	6.49 (6.45)	22.49 (22.58)	80	69
25.	H	CH_3	101	46.21 (46.15)	7.71 (7.69)	35.79 (35.89)	73	68
26.	H	$C_6H_3OHCH_3O$	174	54.51 (54.54)	6.13 (6.06)	21.11 (21.21)	70	62

TABLE—8



Sl. No.	Nature of R	Nature of R′	M.P. °C	%C Found (Reqd.)	%H Found (Reqd.)	%N Found (Reqd.)	% of germination inhibition at 1000 ppm conc.	
							P. oryzae	*H. oryzae*
27.	C_6H_5	C_6H_5	157	69.84 (69.87)	5.91 (5.78)	17.86 (17.98)	100	78
28.	C_6H_5	$C_6H_4NO_2$(o)	208	63.34 (63.28)	5.12 (5.07)	19.12 (19.14)	78	73
29.	C_6H_5	$C_6H_4NO_2$(m)	154	63.18 (63.28)	5.05 (5.07)	19.13 (19.14)	67	64
30.	C_6H_5	$C_6H_4NO_2$(p)	148	63.16 (63.28)	5.17 (5.07)	19.04 (19.14)	100	100
31.	C_6H_5	C_6H_4OH(o)	142	67.14 (67.08)	5.62 (5.59)	17.29 (17.39)	88	76
32.	C_6H_5	C_6H_4OH(m)	126	67.18 (67.08)	5.49 (5.59)	17.34 (17.39)	100	75
33.	C_6H_5	C_6H_4OH(p)	152	67.21 (67.08)	5.52 (5.59)	17.32 (17.39)	100	88
34.	C_6H_5	$C_6H_4CH_3O$	101	67.58 (67.60)	5.73 (5.83)	16.79 (16.90)	100	80
35.	C_6H_5	$C_6H_4N(CH_3)_2$	260	68.21 (68.23)	6.28 (6.27)	19.01 (19.21)	79	76
36.	C_6H_5	C_4H_3O	124	65.63 (65.64)	5.48 (5.47)	18.25 (18.38)	64	63
37.	C_6H_5	$C_6H_3OHCH_3O$	124	65.43 (65.49)	5.72 (5.65)	16.21 (16.37)	66	48
38.	C_6H_5	C_6H_3OHBr	162	57.56 (57.66)	4.58 (4.62)	14.87 (14.94)	67	60
39.	H	C_6H_5	89	57.12 (57.14)	6.13 (6.03)	26.31 (26.66)	60	52
40.	H	$C_6H_4NO_2$(o)	168	50.01 (50.00)	5.20 (5.00)	27.09 (27.22)	62	60
41.	H	$C_6H_4NO_2$(m)	134	50.12 (50.00)	5.17 (5.00)	27.22 (27.22)	78	79
42.	H	$C_6H_4NO_2$(p)	251	50.20 (50.00)	5.08 (5.00)	27.14 (27.22)	46	43
43.	H	C_6H_4OH(o)	214	54.36 (54.38)	5.64 (5.74)	25.32 (25.37)	78	69
44.	H	C_6H_3OHBr	298	43.81 (43.91)	4.29 (4.39)	20.44 (20.49)	60	50
45.	H	$C_6H_2CH_3OBr_2$	292	38.17 (38.18)	3.67 (3.77)	16.62 (16.70)	46	40
46.	H	$C_6H_4N(CH_3)_2$	above 350	56.88 (56.98)	6.59 (6.70)	27.31 (27.37)	68	60
47.	H	C_6H_4Cl	141	51.54 (51.50)	5.23 (5.15)	24.02 (24.03)	70	65
48.	H	$C_6H_4CH_3O$	246	55.52 (55.65)	6.13 (6.08)	24.23 (24.34)	85	49
49.	H	CH_3	258	47.41 (47.43)	6.58 (6.71)	33.17 (33.20)	74	70
50.	H	$C_6H_3OHCH_3O$	278	53.15 (53.18)	5.72 (5.81)	23.06 (23.26)	67	63

temperature. A white compound was formed. On crystallisation from abs. alcohol, white needle-shaped crystals were obtained, m.p. 157°, yield 75%.

The product is soluble in 10% sodium hydroxide and gives colouration with alcoholic ferric chloride.

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Symmetries in New Situations and Their Realisation in Some Systems

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Li's higher order symmetries have been examined in some new situations for transport processes where the total rate processes are obtained by the linear combinations of processes involving unequal order of independence and uneven number of fluxes. Attempt has also been made to examine a few cases of practical interest wherein these symmetries appear to be physically meaningful.

LI'S general symmetry relations[1,2] which follow as a mathematical consequence[3-5] for a general class of linear transformations involving any number of fluxes, so well known in thermodynamics of irreversible processes[6-8], have been discussed by a number of investigators[6,9-11]. Subsequent analysis of the subject in a little more detail has revealed that in addition to the general symmetries envisaged earlier[9-11] there exist some other kind of symmetries also[10,12]. We have named them as special symmetries and the conditions under which these may be realised have also been elaborated[12]. It may be pointed out that some special types of linear combination of the fluxes in question are the prerequisite for the realisation of such special symmetries. We proceed to discuss in the present communication a few implications which arise when the total rate processes are formed by the linear combination of (i) unlike order of independence and (ii) unequal number of fluxes.

Furthermore we also try to point out a few appropriate situations where higher order symmetries are visualised in correct perspectives.

Discussion

It has been shown earlier[11] that if the original rate processes J_i $(i=1, 2, \ldots r)$ with conjugate forces X_i be represented as

$$J_i=\left(\frac{\partial J_i}{\partial X_i}\right)_o X_i+\frac{1}{2!}\left(\frac{\partial^2 J_i}{\partial X_i^2}\right)_o X_i^2+\ldots\ldots \quad \ldots(1)$$

and the total rate processes J'_i as

$$\begin{bmatrix} J'_1 \\ J'_2 \\ \cdot \\ J'_r \end{bmatrix} = \underset{N}{\begin{bmatrix} n_{11} & n_{12} & \ldots & n_{1r} \\ n_{21} & n_{22} & \ldots & n_{2r} \\ \ldots & \ldots & & \ldots \\ n_{r1} & n_{r2} & \ldots & n_{rr} \end{bmatrix}} \begin{bmatrix} J_1 \\ J_2 \\ \cdot \\ J_r \end{bmatrix} \quad \ldots(2)$$

then the new forces X'_i will be given by the following relation :

$$\begin{bmatrix} X_1 \\ X_2 \\ \cdot \\ X_r \end{bmatrix} = \begin{bmatrix} n_{11} & n_{21} & \ldots & n_{r1} \\ n_{12} & n_{22} & \ldots & n_{r2} \\ \ldots & \ldots & \ldots & \ldots \\ n_{1r} & n_{2r} & \ldots & n_{rr} \end{bmatrix} \begin{bmatrix} X'_1 \\ X'_2 \\ \cdot \\ X'_r \end{bmatrix} \quad \ldots(3)$$

and the nth order coefficient L_n by the expression

$$\begin{aligned} L_n = & \quad L\,(11..n)\ \ (22..n)\ \ldots\ (rr\ldots n) \\ = & \left(n_{11}^{n_1}\ n_{21}^{n_2}\ldots n_{r1}^{n_r}\right)\left(\frac{\partial^n J_1}{\partial X_1^n}\right)_o+\left(n_{12}^{n_1}\ n_{22}^{n_2}\ldots n_{r2}^{n_r}\right) \\ & \left(\frac{\partial^n J_2}{\partial X_2^n}\right)_o+\cdots+\left(n_{1r}^{n_1}\ n_{2r}^{n_2}\ \ldots n_{rr}^{n_r}\right)\left(\frac{\partial^n J_r}{\partial X_r^n}\right)_0 \quad \cdots(4) \end{aligned}$$

where $\sum_{i=1}^{r} n_i=n+1$.

We now examine the following situations :

(a) If higher order symmetry relation can exist when unequal number of fluxes are used in the linear combination, i.e., some elements n_{ik}'s are zero in the transformation matrix N.

(b) If the higher order symmetries could be observed when the processes involved in the linear combination have unequal number and different order of independence.

In dealing with the first situation we find that in the event when an element $n_{ik}=0$ the kth term in eq. (4) vanishes in all the nth order coefficients in which the number n_i of the integer i in their subscripts is none—zero. In fact $n_{ik}=0$ implies that the flux J_k has not been included in the linear combination to form the total rate process J'_i. It becomes thus obvious that the exclusion of a flux J_k in the formation of any total rate process makes the kth

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term vanishing only, without in any way affecting the general symmetry relations. This will be true in those situations also where more than one flux are excluded in the transformations resulting in many terms in eq. (4) to vanish. However, if along-with the condition $n_{ik}=0$, $n_i=0$ also holds simultaneously, the situation becomes a little different without producing any substancial effect on the general symmetries. In this situation the kth term will not vanish because of the absence of n_{ik} in eq. (4) and all the nth order coefficients in which integer i is absent, will contain kth term also keeping the general symmetry relations infact.

In dealing with the second situation where linear combinations of processes of unequal number and different order of independence are carried out the independence of the total rate process is governed by the highest order of independence of the processes used in such combinations. As a result of this some of the total rate processes will be associated with greater number of higher order coefficient in comparison to the other ones. But this is expected to be so simply because of the inclusion of some fluxes in some of the total processes and their exclusion from others ; a condition under which we have just discussed above that higher order symmetries remain undisturbed. Thus in the present situation higher order symmetries will remain uneffected.

Let us now examine the implication of imposing the above conditions on special symmetry relations which depend on the odd or even character of n_i. Imposition of the condition $n_{ik}=0$ implies that the kth term in L_n may either be zero or non-zero according as $n_i \neq 0$ or $n_i=0$ respectively. It thereby suggests that the value of L_n will depend on the kind of integer i and not on the character of its number n_i. An extension of this situation on account of the presence of more than one zero element in the matrix of transformation may ultimately lead to circumstances in which special symmetry relation have to depend on the kind of integers present in the subscript of L_n only.

In the subsequent paragraph we first proceed to give an exposition of different facets of the above discussion with a suitable illustration and thereafter discuss some physically meaningful symmetry relations in a few cases of importance and practical interests.

Example : Let us consider three fluxes J_1 of second order independence and J_2 and J_3 each of third order independence. If the new fluxes formed as linear combinations of these fluxes be

$$\begin{aligned} J'_1 &= J_1+J_2+J_3 \\ J'_2 &= J_1+2J_2+0J_3 \\ \text{and } J'_3 &= J_1+0J_2+2J_3 \end{aligned} \qquad \ldots \qquad (a)$$

then transformation matrix N will be represented as

$$\underset{N}{\begin{bmatrix} 1 & 1 & 1 \\ 1 & 2 & 0 \\ 1 & 0 & 2 \end{bmatrix}} \qquad \ldots \qquad (b)$$

Since N is symmetric the original conjugate forces X_1, X_2 and X_3 corresponding to fluxes J_1, J_2 and J_3 in view of eq (3) will be given by

$$\begin{aligned} X_1 &= X'_1+X'_2+X'_3 \\ X_2 &= X'_1+2X'_2+0X'_3 \\ X_3 &= X'_1+0X'_2+2X'_3 \end{aligned} \qquad \ldots \qquad (c)$$

where X'_1, X'_2 and X'_3 are new conjugate forces.

Now on substitution of J_1, J_2 and J_3 by the values of X_1, X_2 and X_3 in terms of new forces in (a) we obtain

$$\begin{aligned} J'_1 = {} & \left\{\left(\frac{\partial J_1}{\partial X_1}\right)_o+\left(\frac{\partial J_2}{\partial X_2}\right)_o+\left(\frac{\partial J_3}{\partial X_3}\right)_o\right\}X'_1+\left\{\left(\frac{\partial J_1}{\partial X_1}\right)_o+2\left(\frac{\partial J_2}{\partial X_2}\right)_o\right\}X'_2+\left\{\left(\frac{\partial J_1}{\partial X_1}\right)_o+2\left(\frac{\partial J_3}{\partial X_3}\right)_o\right\}X'_3 \\ & +\frac{1}{2!}\left\{\left(\frac{\partial^2 J_1}{\partial X_1^2}\right)_o+\left(\frac{\partial^2 J_2}{\partial X_2^2}\right)_o+\left(\frac{\partial^2 J_3}{\partial X_3^2}\right)_o\right\}X'^2_1+\frac{1}{2!}\left\{\left(\frac{\partial^2 J_1}{\partial X_1^2}\right)_o+4\left(\frac{\partial^2 J_2}{\partial X_2^2}\right)_o\right\}X'^2_2+\frac{1}{2!}\left\{\left(\frac{\partial^2 J_1}{\partial X_1^2}\right)_o+4\left(\frac{\partial^2 J_3}{\partial X_3^2}\right)_o\right\}X'^2_3 \\ & +\left\{\left(\frac{\partial^2 J_1}{\partial X_1^2}\right)_o+2\left(\frac{\partial^2 J_2}{\partial X_2^2}\right)_o\right\}X'_1X'_2+\left\{\left(\frac{\partial^2 J_1}{\partial X_1^2}\right)_o+2\left(\frac{\partial^2 J_3}{\partial X_3^2}\right)_o\right\}X'_1X'_3+\left\{\left(\frac{\partial^2 J_1}{\partial X_1^2}\right)_o\right\}X'_2X'_3 \\ & +\frac{1}{3!}\left\{\left(\frac{\partial^3 J_2}{\partial X_2^3}\right)_o+\left(\frac{\partial^3 J_3}{\partial X_3^3}\right)_o\right\}X'^3_1+\frac{1}{3!}\left\{8\left(\frac{\partial^3 J_2}{\partial X_2^3}\right)_o\right\}X'^3_2+\frac{1}{3!}\left\{8\left(\frac{\partial^3 J_3}{\partial X_3^3}\right)_o\right\}X'^3_3+\frac{1}{2!}\left\{2\left(\frac{\partial^3 J_2}{\partial X_2^3}\right)_o\right\}X'^2_1X'_2 \\ & +\frac{1}{2!}\left\{4\left(\frac{\partial^3 J_2}{\partial X_2^3}\right)_o\right\}X'_1X'^2_2+\frac{1}{2!}\left\{2\left(\frac{\partial^3 J_3}{\partial X_3^3}\right)_o\right\}X'^2_1X'_3+\frac{1}{2!}\left\{4\left(\frac{\partial^3 J_3}{\partial X_3^3}\right)_o\right\}X'_1X'^2_3 \end{aligned}$$

$$J'_2=\left\{\left(\frac{\partial J_1}{\partial X_1}\right)_0+2\left(\frac{\partial J_2}{\partial X_2}\right)_0\right\}X'_1+\left\{\left(\frac{\partial J_1}{\partial X_1}\right)_0+4\left(\frac{\partial J_2}{\partial X_2}\right)_0\right\}X'_2+\left\{\left(\frac{\partial J_1}{\partial X_1}\right)_0\right\}X'_3+\frac{1}{2!}\left\{\left(\frac{\partial^2 J_1}{\partial X_1^2}\right)_0+2\left(\frac{\partial^2 J_2}{\partial X_2^2}\right)_0\right\}X'^2_1$$

$$+\frac{1}{2!}\left\{\left(\frac{\partial^2 J_1}{\partial X_1^2}\right)_0+8\left(\frac{\partial^2 J_2}{\partial X_2^2}\right)_0\right\}X'^2_2+\frac{1}{2!}\left\{\left(\frac{\partial^2 J_1}{\partial X_1^2}\right)_0\right\}X'^2_3+\left\{\left(\frac{\partial^2 J_1}{\partial X_1^2}\right)_0+4\left(\frac{\partial^2 J_2}{\partial X_2^2}\right)_0\right\}X'_1X'_2+\left\{\left(\frac{\partial^2 J_1}{\partial X_1^2}\right)_0\right\}X'_1X'_3$$

$$+\left\{\left(\frac{\partial^2 J_1}{\partial X_1^2}\right)_0\right\}X'_2X'_3+\frac{1}{3!}\left\{2\left(\frac{\partial^3 J_2}{\partial X_2^3}\right)_0\right\}X'^3_1+\frac{1}{3!}\left\{16\left(\frac{\partial^3 J_2}{\partial X_2^3}\right)_0\right\}X'^3_2+\frac{1}{2!}\left\{4\left(\frac{\partial^3 J_2}{\partial X_2^3}\right)_0\right\}X'^2_1X'_2$$

$$+\frac{1}{2!}\left\{8\left(\frac{\partial^3 J_2}{\partial X_2^3}\right)_0\right\}X'_1X'^2_2.$$

$$J'_3=\left\{\left(\frac{\partial J_1}{\partial X_1}\right)_0+2\left(\frac{\partial J_3}{\partial X_3}\right)_0\right\}X'_1+\left\{\left(\frac{\partial J_1}{\partial X_1}\right)_0\right\}X'_2+\left\{\left(\frac{\partial J_1}{\partial X_1}\right)_0+4\left(\frac{\partial J_3}{\partial X_3}\right)_0\right\}X'_3$$

$$+\frac{1}{2!}\left\{\left(\frac{\partial^2 J_1}{\partial X_1^2}\right)_0+2\left(\frac{\partial^2 J_3}{\partial X_3^2}\right)_0\right\}X'^2_1+\frac{1}{2!}\left\{\left(\frac{\partial^2 J_1}{\partial X_1^2}\right)_0\right\}X'^2_2+\frac{1}{2!}\left\{\left(\frac{\partial^2 J_1}{\partial X_1^2}\right)_0+8\left(\frac{\partial^2 J_3}{\partial X_3^2}\right)_0\right\}X'^2_3+\left\{\left(\frac{\partial^2 J_1}{\partial X_1^2}\right)_0\right\}X'_1X'_2$$

$$+\left\{\left(\frac{\partial^2 J_1}{\partial X_1^2}\right)_0+4\left(\frac{\partial^2 J_3}{\partial X_3^2}\right)_0\right\}X'_1X'_3+\left\{\left(\frac{\partial^2 J_1}{\partial X_1^2}\right)_0\right\}X'_2X'_3+\frac{1}{3!}\left\{2\left(\frac{\partial^3 J_3}{\partial X_3^3}\right)_0\right\}X'^3_1+\frac{1}{3!}\left\{16\left(\frac{\partial^3 J_3}{\partial X_3^3}\right)_0\right\}X'^3_3$$

$$+\frac{1}{2!}\left\{4\left(\frac{\partial^3 J_3}{\partial X_3^3}\right)_0\right\}X'^2_1X'_3+\frac{1}{2!}\left\{8\left(\frac{\partial^3 J_3}{\partial X_3^3}\right)_0\right\}X'_1X'^2_3.$$

Thus we obtain the following symmetry relations (abbreviations G. S. and S. S. indicate general symmetry and special symmetry respectively) :

	term/terms of		being absent	
$L_{12}=L_{21}=\left(\frac{\partial J_1}{\partial X_1}\right)_0+2\left(\frac{\partial J_2}{\partial X_2}\right)_0$		$\left(\frac{\partial J_3}{\partial X_3}\right)_0$		(G. S.)
$L_{13}=L_{31}=\left(\frac{\partial J_1}{\partial X_1}\right)_0+2\left(\frac{\partial J_3}{\partial X_3}\right)_0$	,, ,,	$\left(\frac{\partial J_2}{\partial X_2}\right)_0$	,,	,,
$L_{23}=L_{32}=\left(\frac{\partial J_1}{\partial X_1}\right)_0$	,, ,,	$\left(\frac{\partial J_2}{\partial X_2}\right)_0$, $\left(\frac{\partial J_3}{\partial X_3}\right)_0$	,,	,,
$L_{112}=L_{211}=\left(\frac{\partial^2 J_1}{\partial X_1^2}\right)_0+2\left(\frac{\partial^2 J_2}{\partial X_2^2}\right)_0$	,, ,,	$\left(\frac{\partial^2 J_3}{\partial X_3^2}\right)_0$	,,	,,
$L_{122}=L_{212}=\left(\frac{\partial^2 J_1}{\partial X_1^2}\right)_0+4\left(\frac{\partial^2 J_2}{\partial X_2^2}\right)_0$	,, ,,	$\left(\frac{\partial^2 J_3}{\partial X_3^2}\right)_0$	,,	,,
$L_{113}=L_{311}=\left(\frac{\partial^2 J_1}{\partial X_1^2}\right)_0+2\left(\frac{\partial^2 J_3}{\partial X_3^2}\right)_0$	,, ,,	$\left(\frac{\partial^2 J_2}{\partial X_2^2}\right)_0$	,,	,,
$L_{123}=L_{213}=L_{312}=L_{233}=\left(\frac{\partial^2 J_1}{\partial X_1^2}\right)_0$	,, ,,	$\left(\frac{\partial^2 J_2}{\partial X_2^2}\right)_0$, $\left(\frac{\partial^2 J_3}{\partial X_3^2}\right)_0$	,,	(S. S.)
$L_{323}=L_{233}=L_{332}=\left(\frac{\partial^2 J_1}{\partial X_1^2}\right)_0$	,, ,,	,, ,,	,,	,,
$L_{133}=L_{313}=\left(\frac{\partial^2 J_1}{\partial X_1^2}\right)_0+4\left(\frac{\partial^2 J_3}{\partial X_3^2}\right)_0$	,, ,,	$\left(\frac{\partial^2 J_2}{\partial X_2^2}\right)_0$	,,	(G. S.)

	term/terms of	being absent	(G. S.)
$L_{1112}=L_{2111}=2\left(\frac{\partial^3 J_2}{\partial X_2^3}\right)_0$	” ” $\left(\frac{\partial^3 J_1}{\partial X_1^3}\right)_0, \left(\frac{\partial^3 J_3}{\partial X_3^3}\right)_0$	”	”
$L_{1122}=L_{2112}=4\left(\frac{\partial^3 J_2}{\partial X_2^3}\right)_0$	” ” $\left(\frac{\partial^3 J_1}{\partial X_1^3}\right)_0, \left(\frac{\partial^3 J_3}{\partial X_3^3}\right)_0$	”	”
$L_{1222}=L_{2122}=8\left(\frac{\partial^3 J_2}{\partial X_2^3}\right)_0$	” ” $\left(\frac{\partial^3 J_1}{\partial X_1^3}\right)_0, \left(\frac{\partial^3 J_3}{\partial X_3^3}\right)_0$	”	”
$L_{1113}=L_{3111}=2\left(\frac{\partial^3 J_3}{\partial X_3^3}\right)_0$	” ” $\left(\frac{\partial^3 J_1}{\partial X_1^3}\right)_0, \left(\frac{\partial^3 J_2}{\partial X_2^3}\right)_0$	”	”
$L_{1133}=L_{3113}=4\left(\frac{\partial^3 J_3}{\partial X_3^3}\right)_0$	” ” $\left(\frac{\partial^3 J_1}{\partial X_1^3}\right)_0, \left(\frac{\partial^3 J_2}{\partial X_2^3}\right)_0$	”	”
$L_{1333}=L_{3133}=8\left(\frac{\partial^3 J_3}{\partial X_3^3}\right)_0$	” ” $\left(\frac{\partial^3 J_1}{\partial X_1^3}\right)_0, \left(\frac{\partial^3 J_2}{\partial X_2^3}\right)_0$	”	”
$L_{1223}=L_{2123}=L_{3122}=L_{1123}=L_{2113}=0$		Non existent	(S. S.)
$L_{3112}=L_{1233}=L_{2133}=L_{3123}=L_{2333}=0$		”	”
$L_{3233}=L_{2233}=L_{3223}=L_{2223}=L_{3222}=0$		”	”

Since $n_{23}=0$ and $n_{32}=0$ in the above transformation matrix N in (b) the coefficients having integer 2 or 3 do not contain the terms with derivatives of J_3 or J_2 respectively and the coefficients having both the integers are free from the terms containing derivatives of J_2 and J_3. Whereas the coefficients free from integer 2 or 3 or both contain terms with derivatives of J_3 or J_2 or both as the case may be. Thus second order coefficients containing integers 2 and 3 show special symmetry relations.

Further as the third order coefficients do not have terms of derivatives of J_1 which has only second order independence, third order coefficients containing both integer 2 and 3 are non-existent.

Thus the results obtained in the above example are in agreement with the theoretical considerations.

Realisation of Symmetries in some Transport Processes :

The most important aspect of the study of higher order symmetries is to find out appropriate situation where they may be found to hold in transport processes. It has been shown[5] by Rastogi et al that such symmetries have physical meaning in some chemical reactions under suitable conditions. However, their presence in other transport processes is still not well recognised and needs proper considerations. In the following lines we would like to point out a few situations where such symmetries in transport processes appear to be physically meaningful.

Electro-kinetics :

In electro-kinetics the electro-osmotic flow J_E and solve dynamic flow J_S together constitute the matter flow J. But from classical theory it is known that electro-osmotic flow J_E is related[14] to current flow I as

$$J_E/I=\frac{\xi D}{4\pi\eta K}=K_1 \text{ or } J_E=K_1 I \qquad \ldots(\text{i})$$

Hence the total matter flow J and current I may be represented by the following linear combinations

$$J=J_S+J_E=J_S+K_1 I \qquad \ldots(\text{ii})$$

$$I=0\ J_S+I \qquad \ldots(\text{iii})$$

If ΔP and $\Delta\varphi$ be the applied pressure and electrical potential respectively then the net electrical potential in the system will be[14] $\Delta\varphi+K_1\Delta P$, where $K_1\Delta P$ is the developed streaming potential. Thus conjugate forces corresponding to fluxes J_S and I are ΔP and $\Delta\varphi+K_1\Delta P$ respectively. The new forces X'_1 and X'_2 corresponding to the total fluxes J and I will, therefore, be given by

$$\begin{bmatrix}\Delta P \\ \Delta\varphi+K_1\Delta P\end{bmatrix}=\begin{bmatrix}1 & 0 \\ K_1 & 1\end{bmatrix}\begin{bmatrix}X'_1 \\ X'_2\end{bmatrix} \ldots(\text{iv})$$

that is $X'_1=\Delta P$ and $K_1X'_1+X'_2=\Delta\varphi+K_1\Delta P$

$$\text{or}\quad X'_2=\Delta\varphi \qquad \ldots(\text{v})$$

Since J_S and I are non-linear in nature they may be written as :

$$J_S = L_{11}\Delta P + \frac{1}{2!}L_{111}(\Delta P)^2 + \frac{1}{3!}L_{1111}(\Delta P)^3 + \ldots \quad \text{(vi)}$$

$$I = L_{22}(\Delta\varphi + K_1\Delta P) + \frac{1}{2!}L_{222}(\Delta\varphi + K_1\Delta P)^2$$

$$+\frac{1}{3!}L_{2222}(\Delta\varphi + K_1\Delta P)^3 + \ldots \quad \ldots\text{(vii)}$$

Using the expressions for J_S and I in eqs. (ii) and (iii) we obtain

$$J = (L_{11} + K_1^2 L_{22})(\Delta P) + K_1 L_{22}(\Delta\varphi)$$

$$+\frac{1}{2!}(L_{111} + K_1^2 L_{222})(\Delta P)^2 + K_1^2 L_{222}(\Delta P)(\Delta\varphi)$$

$$+\frac{1}{2!}K_1 L_{222}(\Delta\varphi)^2 + \ldots \quad \ldots\text{(viii)}$$

$$I = K_1 L_{22}(\Delta P) + L_{22}(\Delta\varphi) + \frac{1}{2!}K_1^2 L_{222}(\Delta P)^2$$

$$+K_1 L_{222}(\Delta P)(\Delta\varphi) + \frac{1}{2!}L_{22}\ (\Delta\varphi)^2 + \ldots \quad \text{(ix)}$$

If J and I represent fluxes 1 and 2 respectively and the primed L's represent their coefficients then we obtain the following symmetries from eqs. (viii) and (ix)

$$L'_{12} = L'_{21} = K_1.L_{22}$$
$$L'_{112} = L'_{211} = K_1^2.L_{222}$$
$$L'_{122} = L'_{212} = K_1.L_{222}\ldots\ldots$$

Thermo-osmosis :

In case of thermo-osmosis the driving force for the elementary flux of matter J_1 is the applied pressure ΔP plus the developed thermo-osmotic pressure $K_1\Delta T$ on account of the temperature difference ΔT in the system and the force corresponding to heat flow J_2 by conduction is ΔT. Since transfer of heat is also caused by the flow of matter the total heat flow H contains this part in addition to J_2. Under these circumstances the total matter flow J and heat flow H may be represented by the following linear combinations of the elementary fluxes J_1 and J_2 :

$$J = J_1 + 0\,J_2 \quad \ldots\text{(i)}$$
$$H = J_1 K_1 + J_2 \quad \ldots\text{(ii)}$$

where $K_1 = S$ (specific heat of the permeant) $\times \Delta T$.

Thus from thermodynamic consideration the conjugate forces X'_1 and X'_2 corresponding to total fluxes J and H will be given by the relation :

$$\begin{bmatrix} \Delta P + K_1\Delta T \\ \Delta T \end{bmatrix} = \begin{bmatrix} 1 & K_1 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} X'_1 \\ X'_2 \end{bmatrix} \quad \text{(iii)}$$

that is $\Delta P + K_1\Delta T = X'_1 + K_1 X'_2$ and $\Delta T = X'_2$

or $X'_1 = \Delta P$ and $X'_2 = \Delta T$ (iv)

In view of Poisiuelle's equation[14] the matter flow J_1 may be written as :

$$J_1 = L_{11}(\Delta P + K_1\Delta T) + \frac{1}{2!}L_{111}(\Delta P + K_1\Delta T)^2 + \ldots \quad \ldots\text{(v)}$$

and further J_2 by Fourier's law of heat conduction as :

$$J_2 = L_{22}(\Delta T) \quad \ldots\text{(vi)}$$

Using these expressions for J_1 and J_2 in eqs. (i) and (ii) we obtain J and H as :

$$J = L_{11}(\Delta P) + K_1 L_{11}(\Delta T)$$

$$+\frac{1}{2!}L_{111}(\Delta P)^2 + K_1 L_{111}(\Delta P)(\Delta T)$$

$$+\frac{1}{2!}K_1^2 L_{111}(\Delta T)^2 + \ldots \quad \ldots\text{(vii)}$$

$$\text{and } H = K_1 L_{11}(\Delta P) + (K_1^2 L_{11} + L_{22})(\Delta T)$$

$$+\frac{1}{2!}K_1 L_{111}(\Delta P)^2 + K_1^2 L_{111}(\Delta P)(\Delta T)$$

$$+\frac{1}{2!}K_1^2 L_{111}(\Delta T)^2 + \ldots \quad \ldots\text{(viii)}$$

From eqs. (vii) and (viii), therefore, in line with electro-kinetics we obtain the following symmetries :

$$L'_{12} = L'_{21} = K_1 L_{11}\ ;\ L'_{112} = L'_{211} = K_1 L_{111}\ ;$$
$$L'_{122} = L'_{212} = K_1^2 L_{111}\ldots\ldots$$

Salt filteration (Electrolyte) :

In case of a Z_2, Z_3 valent electrolytic solution the elementary fluxes which occur in the system are those of molecules of solvent and two types of ionic species. If J_1, J_2 and J_3 respectively denote these fluxes then chemical potential difference of solvent $\Delta\mu_1$ and electro-chemical potential differences $\Delta\tilde{\mu}_2$ and $\Delta\tilde{\mu}_3$ act as driving forces for the respective species. From thermodynamic consideration[15-19] it is known[20] that $\Delta\mu_1 = V_1(\Delta P - \Delta\pi)$, $\Delta\pi$ being the osmotic pressure of the solution and the chemical potential of the salt $\Delta\mu_S$ is related to the electrochemical potentials of the ionic species by the relation[21,22]

$$\Delta\mu_S = \nu_2\Delta\tilde{\mu}_2 + \nu_3\Delta\tilde{\mu}_3 \quad \ldots \quad \text{(i)}$$

where ν_2 and ν_3 are the number of ions which are obtained by the dissociation of one molecule of salt. For electroneutrality

$$\nu_2 Z_2 + \nu_3 Z_3 = 0 \quad \ldots \quad \text{(ii)}$$

Further the e.m.f. $\Delta\varphi$ acting in the system with respect to the electrodes reversible to the ion 2 (say) may be described by

$$\Delta\varphi = \frac{\Delta\tilde{\mu}_2}{Z_2 F} \quad \ldots \quad \text{(iii)}$$

Thus the forces may be conveniently written as

$$\Delta\mu_1 = V_1(\Delta P - \Delta\pi)$$
$$\Delta\tilde{\mu}_2 = Z_2 F \Delta\varphi \qquad \ldots \quad \text{(iv)}$$
$$\Delta\tilde{\mu}_3 = \frac{\Delta\mu_S}{\gamma_3} - \frac{\gamma_2 Z_2 F \Delta\varphi}{\gamma_3} = \frac{\Delta\mu_S}{\gamma_3} + Z_3 F \Delta\varphi$$

Now volume flow J_V electrical current I and salt flow J_S may be obtained as linear combinations of the elementary fluxes J_1, J_2 and J_3 as given under :

$$J_V = J_1 V_1 + J_S V_S = J_1 V_1 + \frac{J_3 V_S}{\gamma_3}$$
$$I = Z_2 F J_2 + Z_3 F J_3$$
$$J_S = \frac{J_3}{\gamma_3}$$

i.e.,

$$\begin{pmatrix} J_V \\ I \\ J_S \end{pmatrix} = \begin{pmatrix} V_1 & 0 & \frac{V_S}{\gamma_3} \\ 0 & Z_2F & Z_3F \\ 0 & 0 & \frac{1}{\gamma_3} \end{pmatrix} \begin{pmatrix} J_1 \\ J_2 \\ J_3 \end{pmatrix} \quad \ldots \text{(v)}$$

where V's stand for molar volumes of the different species.

The conjugate forces X'_1, X'_2 and X'_3 corresponding to these new fluxes, therefore, may be obtained from the relation

$$\begin{pmatrix} V_1(\Delta P - \Delta\pi) \\ Z_2 F \Delta\varphi \\ \frac{\Delta\mu_S}{\gamma_3} + Z_3 F \Delta\varphi \end{pmatrix} = \begin{pmatrix} V_1 & 0 & 0 \\ 0 & Z_2F & 0 \\ \frac{V_S}{\gamma_3} & Z_3F & \frac{1}{\gamma_3} \end{pmatrix} \begin{pmatrix} X'_1 \\ X'_2 \\ X'_3 \end{pmatrix} \quad \ldots \text{(vi)}$$

Thus $V_1 X'_1 = V_1(\Delta P - \Delta\pi)$ or $X'_1 = (\Delta P - \Delta\pi)$

$$Z_2 F X'_2 = Z_2 F \Delta\varphi \quad \text{or} \quad X'_2 = \Delta\varphi \qquad \ldots \quad \text{(vii)}$$

$$\frac{V_S X'_1}{\gamma_3} + Z_3 F X'_2 + \frac{X'_3}{\gamma_3} = \frac{\Delta\mu_S}{\gamma_3} + Z_3 F \Delta\varphi$$

or $X'_3 = (C_S V_S + 1)\frac{\Delta\pi}{C_S} \simeq \frac{\Delta\pi}{C_S}$

[∵ $C_S V_S$ is small for dilute solution and[20]

$\Delta\mu_S = \left(V_S \cdot \Delta P + \frac{\Delta\pi}{C_S}\right)$].

Since the fluxes through membrane capillaries are governed by Poiseuille's equation we may represent J_1, J_2 and J_3 in the power series of forces as :

$$J_1 = L_{11} V_1 (\Delta P - \Delta\pi) + \frac{1}{2!} L_{111} V_1^2 (\Delta P - \Delta\pi)^2 + \ldots$$

$$J_2 = L_{22}(Z_2 F \Delta\varphi) + \frac{1}{2!} L_{222} (Z_2 F \Delta\varphi)^2 + \ldots$$

$$J_3 = L_{33}\left(\frac{\Delta\mu_S}{\gamma_3} + Z_3 F \Delta\varphi\right) + \frac{1}{2!} L_{333}\left(\frac{\Delta\mu_S}{\gamma_3} + Z_3 F \Delta\varphi\right)^2 + \ldots \qquad \ldots \text{(viii)}$$

Inserting these expressions for J_1, J_2 and J_3 in eq. (iv) along with the values of the forces in terms of the new forces from eq. (vii) we obtain

$$\begin{aligned} J_V = {} & \left(V_1^2 L_{11} + \frac{V_S^2}{\gamma_3^2} L_{33}\right)(\Delta P - \Delta\pi) + \frac{V_S Z_3 F}{\gamma_3} L_{33}(\Delta\varphi) + \frac{V_S}{\gamma_3^2} L_{33}\left(\frac{\Delta\pi}{C_S}\right) \\ & + \frac{1}{2!}\left(V_1^2 L_{111} + \frac{V_S^2}{\gamma_3^2} L_{333}\right)(\Delta P - \Delta\pi)^2 \\ & + \frac{1}{2!} \frac{V_S Z_3^2 F^2}{\gamma_3} L_{333}(\Delta\varphi)^2 \\ & + \frac{1}{2!}\frac{V_S}{\gamma_3^3} L_{333}\left(\frac{\Delta\pi}{C_S}\right)^2 + \frac{V_S^2 Z_3 F}{\gamma_3^2} L_{333}(\Delta P - \Delta\pi)(\Delta\varphi) \\ & + \frac{V_S^2}{\gamma_3^3} L_{333}(\Delta P - \Delta\pi)\left(\frac{\Delta\pi}{C_S}\right) \\ & + \frac{V_S Z_3 F}{\gamma_3^2} L_{333}(\Delta\varphi)\left(\frac{\Delta\pi}{C_S}\right) + \ldots \end{aligned} \qquad \ldots \text{(ix)}$$

$$\begin{aligned} I = {} & \frac{Z_3 F V_S}{\gamma_3} L_{33}(\Delta P - \Delta\pi) \\ & + (Z_2^2 F^2 L_{22} + Z_3^2 F^2 L_{33})(\Delta\varphi) + \frac{Z_3 F}{\gamma_3} L_{33}\left(\frac{\Delta\pi}{C_S}\right) \\ & + \frac{1}{2!} \frac{Z_3 F V_S^2}{\gamma_3^2} L_{333}(\Delta P - \Delta\pi)^2 \\ & + \frac{1}{2!}(Z_2^3 F^3 L_{222} + Z_3^3 F^3 L_{333})(\Delta\varphi)^2 \\ & + \frac{1}{2!} \frac{Z_3 F}{\gamma_3^2} L_{333}\left(\frac{\Delta\pi}{C_S}\right)^2 + \frac{Z_3^2 F^2 V_S}{\gamma_3} L_{333}(\Delta P - \Delta\pi)(\Delta\varphi) \\ & + \frac{Z_3 F V_S}{\gamma_3^2} L_{333}(\Delta P - \Delta\pi)\left(\frac{\Delta\pi}{C_S}\right) \\ & + \frac{Z_3^2 F^2 V_S}{\gamma_3} L_{333}(\Delta\varphi)\left(\frac{\Delta\pi}{C_S}\right) + \ldots \end{aligned} \qquad \ldots \text{(x)}$$

$$\begin{aligned} J_S = {} & \frac{V_S}{\gamma_3^2} L_{33}(\Delta P - \Delta\pi) + \frac{Z_3 F}{\gamma_3} L_{33}(\Delta\varphi) \\ & + \frac{1}{\gamma_3^2} L_{33}\left(\frac{\Delta\pi}{C_S}\right) + \frac{1}{2!}\frac{V_S}{\gamma_3^3} L_{333}(\Delta P - \Delta\pi)^2 \\ & + \frac{1}{2!} \frac{Z_3^2 F^2}{\gamma_3} L_{333}(\Delta\varphi)^2 + \frac{1}{2!}\frac{1}{\gamma_3} L_{333}\left(\frac{\Delta\pi}{C_S}\right)^2 \\ & + \frac{V_S Z_3 F}{\gamma_3^2} L_{333}(\Delta P - \Delta\pi)(\Delta\varphi) \\ & + \frac{V_S}{\gamma_3^3} L_{333}(\Delta P - \Delta\pi)\left(\frac{\Delta\pi}{C_S}\right) \\ & + \frac{Z_3 F}{\gamma_3^2} L_{333}(\Delta\varphi)\left(\frac{\Delta\pi}{C_S}\right) + \ldots \end{aligned} \qquad \ldots \text{(xi)}$$

If integers 1, 2 and 3 denote J_V, I and J_S respectively and primed L's stand for their coefficients then from eqs. (ix)-(xi) we obtain the following symmetries:

$$L'_{12}=L'_{21}=\frac{(V_S Z_s F L_{ss})}{\gamma_s};\ L'_{1s}=L'_{s1}=\frac{(V_S L_{ss})}{\gamma_s^2}$$

$$L'_{2s}=L'_{s2}=\frac{(Z_s F L_{ss})}{\gamma_s}$$

$$L'_{112}=L'_{211}=\frac{(V_S^2 Z_s F L_{sss})}{\gamma_s^2};$$

$$L'_{122}=L'_{212}=\frac{(V_S Z_s^2 F^2 L_{sss})}{\gamma_s}$$

$$L'_{113}=L'_{311}=\frac{(V_S^2 L_{sss})}{\gamma_s^3};\ L'_{133}=L'_{313}=\frac{(V_S L_{sss})}{\gamma_s^3}$$

$$L'_{123}=L'_{213}=L'_{312}=\frac{(Z_s F V_S L_{sss})}{\gamma_s^2};\ \ \ldots\ldots$$

Salt filteration (Non-electrolyte) :

In case of a non-electrolytic solution under the gradient of pressure and chemical potential it is invariably found that salt filteration can occur through membrane of wide pore size capillaries and, therefore, the process is different from mechanical sieving effect.

From thermodynamic consideration it is known that driving forces for the fluxes of solvent J_W and solute J_S are their chemical potentials :

$$\Delta\mu_W=V_W(\Delta P-\Delta\pi),\quad \Delta\mu_S=\left(V_S\Delta P+\frac{\Delta\pi}{C_S}\right) \quad \ldots(i)$$

respectively. The different quantities involved in eq. (i) have their usual significance.

Since the flow of matter in a capillary tube is governed by Poiseuille's equation the fluxes $J_1=J_W V_W$ and $J_2=J_S V_S$ may be represented as :

$$J_1=L_{11}(\Delta P-\Delta\pi)+\frac{1}{2!}L_{111}(\Delta P-\Delta\pi)^2 +\frac{1}{3!}L_{1111}(\Delta P-\Delta\pi)^3+\ldots$$

$$J_2=L_{22}\left(\Delta P+\frac{\Delta\pi}{C_S V_S}\right)+\frac{1}{2!}L_{222}\left(\Delta P+\frac{\Delta\pi}{C_S V_S}\right)^2 +\frac{1}{3!}L_{2222}\left(\Delta P+\frac{\Delta\pi}{C_S V_S}\right)^3+\ldots \quad \ldots(ii)$$

Now we obtain the following fluxes as linear combination of J_1 and J_2

$$J'_1=J_1+J_2 \text{ or } J'_2=0J_1+J_2 \quad \begin{bmatrix}J'_1\\J'_2\end{bmatrix}=\begin{bmatrix}1&1\\0&1\end{bmatrix}\begin{bmatrix}J_1\\J_2\end{bmatrix} \quad \ldots(iii)$$

where J'_1 is total volume flow and J'_2 is volume of salt flow.

The corresponding conjugate forces X'_1 and X'_2 of these new fluxes will, therefore, be given by the relation

$$\begin{bmatrix}\Delta P-\Delta\pi\\ \Delta P+\frac{\Delta\pi}{C_S V_S}\end{bmatrix}=\begin{bmatrix}1&0\\1&1\end{bmatrix}\begin{bmatrix}X'_1\\X'_2\end{bmatrix} \quad \ldots(iv)$$

i.e., $X'_1=\Delta P-\Delta\pi$,

$$\text{and } X'_2=(C_S V_S+1)\frac{\Delta\pi}{C_S V_S}=\frac{\Delta\pi}{C_S V_S} \quad \ldots(v)$$

Inserting the expressions for J_1 and J_2 from eq. (ii) into eq. (iii) along with the values of forces in terms of new forces from eq. (v) we obtain

$$\begin{aligned}J'_1=&(L_{11}+L_{22})(\Delta P-\Delta\pi)+L_{22}\left(\frac{\Delta\pi}{C_S V_S}\right)\\ &+\frac{1}{2!}(L_{111}+L_{222})(\Delta P-\Delta\pi)^2\\ &+L_{222}(\Delta P-\Delta\pi)\left(\frac{\Delta\pi}{C_S V_S}\right)+\frac{1}{2!}L_{222}\left(\frac{\Delta\pi}{C_S V_S}\right)^2\\ &+\frac{1}{3!}(L_{1111}+L_{2222})(\Delta P-\Delta\pi)^3\\ &+\frac{1}{2!}L_{2222}(\Delta P-\Delta\pi)^2\left(\frac{\Delta\pi}{C_S V_S}\right)\\ &+\frac{1}{2!}L_{2222}(\Delta P-\Delta\pi)\left(\frac{\Delta\pi}{C_S V_S}\right)^2\\ &+\frac{1}{3!}L_{2222}\left(\frac{\Delta\pi}{C_S V_S}\right)^3+\ldots\end{aligned} \quad \ldots(vi)$$

$$\begin{aligned}J'_2=&L_{22}(\Delta P-\Delta\pi)+L_{22}\left(\frac{\Delta\pi}{C_S V_S}\right)\\ &+\frac{1}{2!}L_{222}(\Delta P-\Delta\pi)^2+L_{222}(\Delta P-\Delta\pi)\left(\frac{\Delta\pi}{C_S V_S}\right)\\ &+\frac{1}{2!}L_{222}\left(\frac{\Delta\pi}{C_S V_S}\right)^2+\frac{1}{3!}L_{2222}(\Delta P-\Delta\pi)^3\\ &+\frac{1}{2!}L_{2222}(\Delta P-\Delta\pi)\left(\frac{\Delta\pi}{C_S V_S}\right)\\ &+\frac{1}{2!}L_{2222}(\Delta P-\Delta\pi)\left(\frac{\Delta\pi}{C_S V_S}\right)^2\\ &+\frac{1}{3!}L_{2222}\left(\frac{\Delta\pi}{C_S V_S}\right)^3+\ldots\end{aligned} \quad \ldots(vii)$$

If primed L's denote the coefficients of J'_1 and J'_2 we obtain the following symmetries from eqs. (vi) and (vii) :

$$L'_{12}=L'_{21}=(L_{22})=L'_{22}$$
$$L'_{112}=L'_{211}=(L_{222})=L'_{122}=L'_{212}=L'_{222}$$
$$L'_{1112}=L'_{2111}=(L_{2222})=L'_{1122}=L'_{2112}$$
$$=L'_{1222}=L'_{2122}=L'_{2222}\ldots\ldots$$

Since $n_{21}=0$ in the transformation matrix in eq. (iv) coefficients L_{11}, L_{111}, $L_{1111}\ldots\ldots$ contain two

terms and the special symmetries are independent of the characters of integers 1 and 2. Thus we find that all the coefficients containing integers 1 and 2 or 2 only are equal.

From what has been discussed above it would be clear that the higher order symmetries can be visualised with full physical significance in a number of transport processes. The crux of the problem appears to be the identification of the fluxes and forces in the process of linear combinations of the original fluxes and forces in a correct perspective. Once this has been achieved the higher order symmetries appear to follow naturally like a logical consequence.

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NOTES

Syntheses of New Oxovanadium(IV) Complexes with Tridentate Dibasic Schiff bases Derived from Salicylaldehyde, Substituted Salicylaldehyde and Orthohydroxybenzylamine

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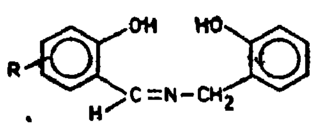
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THE tridentate dibasic ligands yield metal complexes which usually show novel spectral, magnetic and structural properties[1,2]. Recently there has been considerable interest on the syntheses and magnetic properties of oxovanadium(IV) and copper(II) complexes of tridentate dibasic Schiff bases derived from salicylaldehyde or substituted salicylaldehyde and orthoaminophenol or orthoaminothiophenol[3-5]. In this preliminary communication the syntheses of a few new oxovanadium(IV) complexes of tridentate dibasic Schiff bases (I) derived from salicylaldehyde or substituted salicylaldehyde and orthohydroxybenzylamine are reported. Only the dioxouranium(VI) complexes of I have recently been described[6].



I

Method of preparation of the complexes :

A solution of the appropriate Schiff base (0.005*M*) was prepared by refluxing salicylaldehyde or substituted salicylaldehyde (0.005 *M*) in 50 ml of methanol. To this solution a methanolic solution of freshly prepared vanadyl acetate (0.005 *M* in 20 ml) was added slowly with stirring. The mixture was refluxed for 2 hrs. with stirring. The separated precipitates were filtered, washed with methanol and dried under vacuum. The characterisation data of the complexes are given in Table 1.

The analytical data indicate metal : ligand ratio, 1 : 1 for all the complexes. The infrared spectra of the complexes show the absence of ν(OH) stretch. This is indicative of coordination of phenolic oxygens to VO(IV) and the dibasic character of these Schiff bases. The ν(V=O) stretch of the complexes is given in Table 1 and this occurs in the range 900-910 cm^{-1} which is in the usual range observed for the majority of oxovanadium(IV) complexes[2,7]. The complexes are insoluble in common solvents and decompose or melt above 250°. The ligands I behave as tridentate dibasic ligands and this requires that these oxovanadium(IV) complexes will be dimeric or polymeric in order to achieve the normal penta-coordination. The insolubility of the complexes prevented the molecular weight determination of the complexes. The magnetic moments of the complexes were determined at room temperature by the Gouy method using $Hg[Co(NCS)_4]$ as the standard. The complexes exhibit the room temperature magnetic moments in the range 1.1-1.2 B.M. which is significantly lower than the spin—only value of 1.73 B.M. expected for magnetically dilute oxovanadium(IV) complexes ($S=\frac{1}{2}$). The low magnetic moment in these complexes indicates the

TABLE 1—THE ANALYTICAL, MAGNETIC MOMENT AND V=O FREQUENCY DATA OF OXOVANADIUM(IV) COMPLEXES[a]

Complex		%V	%N	μ_{eff} B.M.	ν(V=O)[b] cm^{-1}
VO(sal-*o*-hydroxybenzylamine)	Found :	17.1	4.4	1.11	910
	Calcd :	17.47	4.79		
VO(5-chlorosal-*o*-hydroxybenzylamine)	Found :	14.9	4.2	1.19	905
	Calcd :	15.63	4.29		
VO(5-bromosal-*o*-hydroxybenzylamine)	Found :	13.4	3.9	1 18	910
	Calcd	13.75	3.77		
VO(3, 5-dichlorosal-*o*-hydroxybenzylamine)	Found :	14.1	3.5	1.11	910
	Calcd :	14.13	3.88		
VO(4-methoxysal-*o*-hydroxybenzylamine)	Found :	15.4	4.1	1.23	900
	Calcd :	14 84	4.35		
VO(hydrox-*o*-hydroxybenzylamine)	Found :	14.5	3.8	1.10	910
	Calcd :	14.91	4.09		

(a) Abbreviations : sal = salicylaldehyde, 5-chlorosal = 5-chlorosalicylaldehyde, 5-bromosal = 5-bromosalicylaldehyde, 3, 5-dichlorosal = 3, 5-dichlorosalicylaldehyde, 4-methoxysal = 4-methoxysalicylaldehyde and hydrox = 2-hydroxy-1-naphthaldehyde.

(b) The infrared spectra were recorded on a Perkin-Elmer Model 237 infrared spectrophotometer in KBr pellets.

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spin-spin coupling in the interacting vanadium atoms and the exchange interaction is of the antiferromagnetic type with singlet ground state[2,3].

The low temperature magnetic and electron spin resonance studies of the complexes are progressing and details will be reported in due course. The corresponding oxomolybdenum(V), oxotungsten(V) and copper(II) complexes are also being studied in order to compare the magnetic exchange behaviour of these $S=\frac{1}{2}$ systems. The syntheses of coordination complexes of various other transition and non-transition metal ions with I are being carried out.

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Dissociation Constants of 1, 10-Phenanthroline and its Iron(II) Complex in Ethanol and Water Mixtures

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IN order to explore the role of the solvents on the dissociation constants of the complexes, we studied the dissociation constants of the following 'iso-electric' equilibria in ethanol+water mixtures. (Containing 8-87 wt% of ethanol)

$$PhH^+ \rightleftharpoons Ph + H^+ \quad \dots (1)$$
$$FePh_3^{2+} + 3H^+ \rightleftharpoons Fe^{2+} + 3PhH^+ \quad \dots (2)$$
$$FePh_3^{2+} \rightleftharpoons Fe^{2+} + 3Ph \quad \dots (3)$$

The thermodynamics of reaction (1) have been reported. We report in this communication the equilibrium constants for reactions (2) and (3) in ethanol+water mixtures.

Methods and Materials

The purification of the solvent, the preparation of ferrous-ammonium-sulphate and 1, 10-phenanthroline solutions, the determination of the weight percentages of the organic solvents in the mixed solvents and their dielectric constants were done in the way described before[1-3].

The chemicals used were of G.R. grade. Double-distilled water was used for preparing the solutions.

The organic solvent has been found to have little effect on the absorption maximum of ferroin which is 510 nm. Under our experimental conditions, $FePh_3^{2+}$ has been assumed to be the sole species formed without any $FePh^{2+}$ and $FePh_2^{2+}$.

The molar absorptivities ϵ's of ferroin were determined at 500, 510 and 520 nms from the measurement of absorbances of solutions containing more than 10 fold excess of ligand to known amounts of ferrous ion where complete conversion of Fe^{2+} to $FePh_3^{2+}$ took place.

For the determination of stability constants of ferroin in mixed solvents, absorbances of solutions containing different amounts of Fe^{2+} ion and 1, 10-phenanthroline (Concn. range $8\text{-}20\times10^{-5}M$) were measured at 500, 510 and 520 nms. The *p*Hs ranged from 2.60-3.80.

For the calculation of equilibrium constants for the reactions (2) and (3), the average values of the complex obtained from absorbance measurements and ϵ values at three wavelengths were taken.

Spectrophotometric readings were taken with a Beckman DU Spectrophotometer maintained at 25°. The *p*H-meter readings were taken with a Cambridge-bench type battery operated *p*H-meter.

Results

In mixed solvents, the activity coefficients change due to

(i) Salt effect $({}_sf_i)$, (ii) Medium effect $({}_mf_i)$. Salt effect may be eliminated by working in very dilute solutions so that

${}_sf_i \rightarrow 1$, i.e. ${}_sf_{Fe^{2+}} = {}_sf_{FePh_3^{2+}}$ and ${}_sf_{H^+} = {}_sf_{PhH^+}$. This enables us to get an idea regarding 'medium effect' with which we are concerned in our studies in mixed solvents. Furthermore, addition of inert electrolyte or increase in the concentrations of reactions would lead to further complications due to

(a) ion-association,

(b) Solute-solvent interactions and preferential solvation of ions in mixed solvents.

Considering these facts, the present work has been carried out in solutions of the order of $10^{-5}M$ (ionic strengths were of the order of 4.0×10^{-4} to $3.3\times10^{-5}M$).

The thermodynamic equilibrium constant K_a for reaction (2) has been calculated from

$$(PhH^+) = (Ph)_{total} - 3(FePh_3^{2+}) - (Ph) \quad \ldots \quad (4)$$

$$pK_T = pH + \log\frac{(PhH^+)}{(Ph)} \quad \ldots \quad (5)$$

$$\text{and } (Fe^{2+})_{free} = (Fe^{2+})_{total} - (FePh_3^{2+}) \quad \ldots \quad (6)$$

We prefer to use the theoretical values of H^+ ion concentrations in calculating the K-values in view of increasing discrepancy of the theoretical and experimental values of H^+ ion concentrations (as measured pH-metrically using appropriate correction[4]) as the percentage of organic solvent increases. This is expected in mixed solvents with ions of different charge types due to

(1) liquid-junction potential of uncertain magnitude,

(2) change in sensitivity of the electrode,

(3) solute-solvent interactions and consequent medium effect.

The dissociation constant for the reaction (3) in different solvents are given by

$$K = K_a \times K_T^3 \quad \ldots \quad (7)$$

Discussions

The pK values for the reactions (1), (2) and (3) at different percentages of mixed solvents are given in Table 1.

TABLE—1

Wt. % of ethanol	Mole-frac. of ethanol	$1/\epsilon\times10^2$	pK_T for reacn. (1) Spectro-photomet.	pH-metry	Extinction Coefficients of Ferroin 500 nm	510 nm.	520 nm	pK_a for reacn(2)	pK for reacn.(3)
0	0.000	1.27	5.05[a]	–				5.35	20.50[a]
8.0	0.033	1.35	4.90	4.82	10578(±15)	10780(±15)	9792(±15)	5.30	19.76
16.4	0.071	1.42	4.75	4.70	10760	10920	9830	5.12	19.22
25.8	0.117	1.53	4.50	4.41	11500	11710	10540	4.96	18.59
34.4	0.170	1.71	4.34	4.27	11760	11910	10820	5.54	18.35
44.0	0.235	1.90	4.05	4.03	11600	11780	10510	5.21	17.30
54.1	0.315	2.14	3.82	3.89	11170	11500	11020	5.08	16.70
64.7	0.418	2.45	3.08	3.77	10810	11260	10640	5.61	16.92
76.0	0.554	2.92	3.62	3.70	10610	11000	10460	5.44	16.54
87.6	0.754	3.41	3.70	–	10600	10956	10890	5.08	16.13

The plots of pK values against mole-fraction and $1/\epsilon$ give linear plots nearly up to 65 per cent. of organic solvent within the limits of experimental error.

It is to be noted that slight error in the measurement of H^+ ions (±0.04) will have profound effect on K_a and K. Moreover, the solute-solvent interactions in mixed solvents with ions and complexes of higher valence types may have influence on the equilibrium constants. Considering the limitations, the results can be regarded to be in good agreement.

In consistence with the previous observations it has been found that solute-solvent interactions are the major terms to explain the solvent-effect,[1-3,5] the electrostatic terms being of minor importance due to 'isoelectric' nature of the reactions. Greater solubility of 1, 10-phenanthroline in mixed solvents and the differences in the solvational properties of H^+, PhH^+, $FePh_3^{2+}$ and Fe^{2+} are partly responsible for the change in pK values. However, the nature of solvation are not clear but it is likely that Fe^{2+} and H^+ ions would be preferentially solvated by water molecule compared to PhH^+ and $FePh_3^{2+}$ due to bigger ion-sizes.

The pK_T values for reaction (1) show a minimum in the region 65-75 wt.% of organic solvents by spectrophotometry. The pK_a values for the reaction (2) are peculiar showing abnormality near about 25 and 54 wt.% of alcohol. For reaction (3), the pK-values decrease as the alcohol content increases. Slight deviation is noted near about 65 wt.% The 'correction factor' were maximal near about 65 wt% . The changes in molar absorptivities with increasing alcohol though interesting but cannot be correlated with the other data obtained.

It is known that $\Delta pK = \Delta pK_{el} + \Delta pK_{nonel}$. But for the 'isoelectric' reactions, ΔpK_{el} may be assumed to be almost constant as a first approximation throughout the solvent composition. Thus, the change in pK represent primarily the change in ΔpK_{nonel} which is governed to a large extent by solute-solvent in interactions and solvent basicity which are probably maximum in the region of 60-80 wt.% of ethanol.

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Studies on Some Mixed-ligand Complexes of Tin Tetrachloride

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IN continuation to our studies on mixed-ligand complexes[1] we wish to report synthesis and characterisation of a few more hitherto unknown complexes of similar general formula $SnCl_4$. LL′(L= dimethyl formamide (DMF), dimethyl acetamide (DMA), dimethyl propionamide (DMP), or diphenylformamide (DPF) ; L′= pyridine N-oxide (PyO) or lutidine N-oxide (TNO). Possible structure of the complexes is suggested.

Experimental

Materials : Commercially available tin tetrachloride was used after distillation. DMF, DMA, DMP, DPF, PyO and LNO were obtained from Fischer Scientific U. S. A. and used as such.

Preparation of complexes : The mixed-ligand complexes were prepared according to one of the following methods :

(i) Displacement reaction :

$$SnCl_4 . 2L + L' \rightarrow SnCl_4 . LL' + L$$

In a representative experiment a solution of 2 m moles of $SnCl_4$. 2DMF in 10 ml. acetonitrile was treated with an equimolar quantity of PyO in the same solvent. The mixture was refluxed for about two hours and the excess solvent was distilled off. The residual solution on treatment with diethyl ether yielded a white crystalline solid which was filtered, washed and dried in vacuum.

(ii) Adduct formation :

$$SnCl_4 + L + L' \rightarrow SnCl_4 LL'$$

A solution of 5 m moles of tin tetrachloride in 10 ml carbon tetrachloride was treated with an equimolar mixture of DMF and PyO (5 m mole each) in 10 ml of the same solvent with constant stirring. The precipitated white crystalline solid was identical to that obtained through displacement reaction.

The experimental results are collected in Table 1.

Results and Discussion

The newly synthesised compounds are white crystalline solid having poor solubility in organic solvents. They are non-electrolytes, thermally stable and unaffected by atmospheric moisture and oxygen.

The IR spectral data show a distinct negative shift of the C=O stretching frequency and a slight positive shift of the NCO bending mode from their position in the free ligands, in agreement to the observations of previous workers[2-5], and indicate the coordination from the oxygen atom of the amide molecule to the tin atom. The presence of coordinated N=O ligands through the oxygen atom is indicated from the following[6-9] :

(a) The N=O str. mode around 1185 ± 5 cm^{-1} is distinctly shifted to lower frequency region as compared to that in the free bases.

(b) The N=O bending mode appears at 832 ± 3 cm^{-1} in the complexes. Its location is not very different from that in the corresponding bases which is in agreement to the observations and explanations of several previous workers.

TABLE 1—ANALYTICAL RESULTS AND IR ABSORPTION FREQUENCIES (cm^{-1}) FOR $SnCl_4$.LL′

L	L′	Analysis % obs. (calcd.) Sn	C	H	N	IR absorption frequencies (cm^{-1}) Amide I band ν(C=O)	δ(N−C=O)	ν(N−O)	δ(N−O)	ν(O−H)	(ν(Sn−O)
DMF	PyO	26.80 (27.71)	20.30 (20.21)	2.82 (2.81)	6.40 (6.31)	1610 m	670 vs	1180 s	830 vs	780 vs	400 m 330 m
DMA	PyO	26.40 (26.80)	24.62 (24.38)	3.38 (3.19)	6.50 (6.25)	1610 m	675 vs	1180 m	830 vs	780 vs	390 m 335 m
DMP	PyO	25.60 (25.28)	28.20 (28.02)	3.78 (3.80)	6.00 (5.98)	1620 vs	670 s	1190 m	835 sh	775 vs	390 vs 310 m
DPF	PyO	21.90 (21.58)	39.30 (39.04)	3.44 (3.80)	5.50 (5.38)	1615 m	690 m	1190 m	830 vs	775 s	390 vs 320 m
DMF	LNO	26.00 (26.04)	26.28 (26.20)	3.80 (3.58)	6.80 (6.59)	1610 m	710 m	1185 s	832 m	790 s	410 w 380 s
DMA	LNO	25.60 (25.28)	28.03 (28.02)	3.58 (3.80)	5.58 (5.90)	1615 m	700 m	1190 m	835 m	790 s	400 m 380 m
DMP	LNO	23.60 (23.70)	31.50 (31.19)	4.80 (4.58)	5.50 (5.00)	1620 m	680 m	1182 s	832 m	780 s	390 m 320 w
DPF	LNO	20.80 (20.48)	41.60 (41.36)	3.60 (3.48)	4.60 (4.80)	1612 m	690 vs	1180 m	834 vs	790 vs	410 w 375 m

(c) The C—H out of plane deformation mode identified at 782 ± 8 cm^{-1} shows a positive shift due to tightening of the aromatic ring on complexation.

The two absorptions close to each other in the range 400 – 310 cm^{-1} have been attributed to ν(Sn – O) giving unequivocal support to coordination through the oxygen atoms of the ligands. The appearance of two Sn – O str. modes is an indication of the different bond strength of the Sn – O linkages, consequently suggesting different basicity of the two donor molecules.

Since in hexa coordinated adducts of tin tetrachloride of the formula $SnCl_4.2L$, the two monodentate bases occupy *cis* position, the displacement of one of the ligands by another strong base is not expected to produce a major change in the stereochemistry of the adducts.

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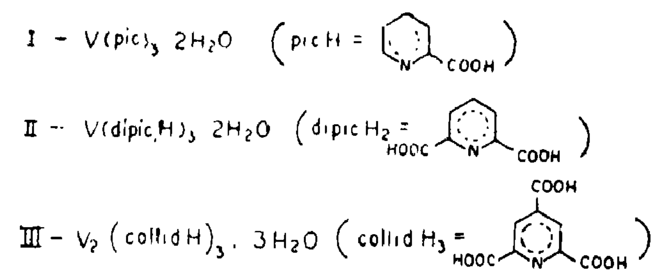
New Stable Vanadium(III) Chelates of Some Pyridine Carboxylic Acids

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TRIVALENT vanadium chelates stable in laboratory atmosphere in solid state as well as in solution are of rare occurrence[1-3]. The present study is undertaken as a part of our programme on stabilization of normally unstable oxidation states of transition metal ions through ligation to suitable donor molecules. Three extremely stable vanadium(III) complexes of pyridine-2-carboxylic acid, pyridine-2, 6-dicarboxylic acid and pyridine-2, 4, 6-tricarboxylic acid are obtained in the solid state. Hot aqueous solution of the ligands (3.25 m moles) are treated with solid VCl_3 (1 m mole) and stirred vigorously when the following compounds are obtained in good yield :



The compounds are washed with boiled out water and alcohol nearly dried under suction and kept over fused calcium chloride for 48 hours.

Elemental analysis is in accordance with the proposed formulation and is given along with the magnetic moment values at room temperature in Table 1. All the three compounds are stable towards oxidation in the solid state. Solutions of the complexes in boiled out water containing small quantities of the appropriate ligands are fairly stable as is indicated from the unchanged nature of their absorption spectra even after two hours. All the compounds can be recrystallised from concentrated aqueous solutions containing some ligand.

Magnetic moment values at room temperature (300°K) given in Table 1 indicate the presence of two unpaired electrons[3,4,5] in all of them. Electronic spectra of the complexes in alcohol and in water in presence of a small amount of the appropriate ligand exhibit two electronic transitions [27000-25000 cm^{-1} : $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$; 13900-12000 cm^{-1} : $^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$] which are indicative of an octahedral disposition of the donor sites around the d^2 V(III) species[1,2,6,7].

I.R. spectra of the ligand and the complexes were monitored in the 4000-250 cm^{-1} region in CsBr-matrix. Both pyridine-2, 6-dicarboxylic acid and pyridine-2, 4, 6-tricarboxylic acid exhibited the –COO stretch as a strong band at 1720-1715 cm^{-1} region and pyridine-2-carboxilic acid exhibited the same stretching mode at 1710 cm^{-1}. In the I.R. spectra of the complexes this 1720-1710 cm^{-1}, band is shifted towards lower wave number region (1675-1665 cm^{-1}) which is indicative of bonding through the carboxyl moiety[8].

In pyridine derivatives the two bands at 600-640 cm^{-1} (in plane ring deformation) and at (400-415 cm^{-1} (out of plane ring deformation) are

TABLE—1

Sl. No.	Compound	Colour	Vanadium		Nitrogen		μ_{eff} at 300°K (B. M.)
			Found %	Required %	Found %	Required %	
I	$V(pic)_2 \cdot 2H_2O$	Orange	11.20	11.26	9.19	9.27	2.78
II	$V(dipic)_2 \cdot 2H_2O$	Yellowish green	8.64	8.76	7.30	7.21	2.66
III	$V_2(collidH)_3 \cdot 3H_2O$	Orange yellow	12.96	13.02	5.42	5.36	2.60

shifted to higher frequency region upon coordination of the ring nitrogen to a metal ion[9,10]. In the I.R. spectra of all the three complexes these bands were shifted to higher frequency region by 20-35 wave numbers and this has been considered as an evidence of coordination through the heterocyclic nitrogen. The presence of lattice water is exhibited by rather broad bands in the 3500-3200 cm^{-1} region[11].

The above facts indicate that the d^2 V(III) entity is present in an octahedral donor environment in all the three chelates. To our knowledge these are among the few examples of V(III) chelates which are stable towards oxidation in open atmospheric conditions.

Further studies on the magnetic behaviour at low temperature structure in the solid state and reactivity of the complex species towards various oxidising agents are in progress.

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Study of Some Binary and Ternary Complexes of Praseodymium(III) with Substituted Salicylic Acids

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IN our earlier communications[1,2] we have described investigations on the binary and ternary complexes of Pr(III) with polyhydroxy phenolic ligands. In the present communication we are reporting for the first time the metal-ligand stability constants of ternary complexes (MAL), where M=Pr(III), A= Nitrilotriacetic acid (NTA) or N-Hydroxyethylethylenediaminetriacetic acid (HEDTA) or Ethylenediaminetetraacetic acid (EDTA) as primary ligand and L-Sulphosalicylic acid (SSA) and 3,5-Dinitrosalicylic acid (DNSA) as secondary ligand (L), by using the modified form of Irving and Rossotti titration technique.

Experimental

The details of the preparation of metal and primary ligand solutions and the instruments used are the same as described in our earlier communications[1,2]. 0.02M solutions of SSA and DNSA were prepared by dissolving requisite quantities in doubly distilled water, and standardized potentiometrically.

The procedure employed and conditions maintained and the methods of calculations used are also the same as described earlier[1,2].

Results and Discussion

Proton-ligand Stability Constants

The formation curves drawn between $\bar{n}_A$ against pH are found to be extended between 0 to 2 for SSA and 0 to 1 for DNSA in the $\bar{n}_A$ scale indicating the early dissociation of $-SO_3H$ group in SSA and $-COOH$ group in DNSA. The obtained are summarised in Table 1.

Metal-ligand Stability Constants of Binary Complexes

For SSA system the formation curves are found to be extended between 0 to 3 in $\bar{n}_A$ scale indicating

the formation of three stepwise complexes between Pr(III) and SSA. In case of DNSA the precipitation was observed at pH 6.0. The calculation of $\bar{n}$ was done using data below the pH of precipitation and the formation curve were found to be extended between 0 to 1 indicating the formation 1 : 1 Pr(III)-DNSA complex. The values obtained for log K are summarised in Table 1.

TABLE 1—PROTON-LIGAND AND METAL-LIGAND STABILITY CONSTANTS OF COMPLEXES

μ = 0.2M AT 25°

System	Constant	Method A	Method B
H-SSA	$\log K_1^H$	11.66	11.62
	$\log K_2^H$	2.47	2.42
H-DNSA	$\log K^H$	7.08	7.07
	$\log K_1$	6.81	6.80
Pr(III)-(SSA)	$\log K_2$	5.66	5.64
	$\log K_3$	3.63	3.61
Pr(III)-(DNSA)	$\log K$	4.94	4.93
Pr(III)-(NTA)(SSA)	$\log K_{MAL}^{NTA}$	6.24	6.28
Pr(III)-(HEDTA)(SSA)	$\log K_{MAL}^{HEDTA}$	4.94	4.96
Pr(III)-(EDTA)(SSA)	$\log K_{MAL}^{EDTA}$	4.44	4.41
Pr(III)-(NTA)(DNSA)	$\log K_{MAL}^{NTA}$	3.46	3.50
Pr(III)-(HEDTA)(DNSA)	$\log K_{MAL}^{HEDTA}$	3.34	3.40
Pr(III)-(EDTA)(DNSA)	$\log K_{MAL}^{EDTA}$	3.18	3.13

Method A = Interpolation at half $\bar{n}(\bar{n}_A)$ values.
B = Interpolation at different $\bar{n}(\bar{n}_A)$ values.

Metal-ligand Stability Constants of Mixed-ligand Complexes

The values of log K_{MAL}^{A} were evaluated by pointwise calculations of $\bar{n}$ and pL, where $\bar{n}$ is the average number of secondary ligands (L) attached per molecule of primary complex Pr(III)-(A). The values obtained for log K_{MAL}^{A} for various systems are summarised in Table 1.

The values of ternary complex formation constants for SSA are higher than DNSA. It has been observed that in cases where A = NTA, HEDTA, log K_{MAL}^{A} is significantly lower than log K_{ML_1}. This is in good agreement with the results reported earlier[1,2] by us with different secondary ligands. This can be explained on the basis that in case of binary complex formation ligand (L) has to approach a positively charged Pr(III) ion and more coordination positions are available for its attachment which results in K_{ML_1} K_{MAL}^{A}. NTA acts as tetra, HEDTA as penta and EDTA as hexa dentate ligand with Pr(III) ion, so lesser number of coordination positions are available for secondary ligand (L) in case of EDTA than with HEDTA, than with NTA system, which results in lowering of stabilities of respective ternary chelates. In case of NTA and HEDTA systems in the secondary ligand (L) has to approach the neutral species Pr(III)-(A). Whereas in case of EDTA system it has to approach a negatively charged Pr(III)-(A) species. This electrostatic effect (repulsion) also results in lowering the values of K_{MAL}^{A} in case of EDTA.

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Preparation and Characterisation of 12-Heteropoly Tantalatomolybdate(VI)

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EXTENSIVE X-ray studies of the aqueous solution of potassium hexatantalate[1-3] showed the existence of polynuclear oxoanions $[HTa_6O_{19}]^{7-}$ and $[Ta_6O_{19}]^{8-}$. Hence it is likely that the heteropolytantalate can be prepared. Dale et al[4] have reported sodium 12-niobotantalatomanganate(IV) and have not found the works of Lapitsku and his coworkers[5] to be reproducible in this connection. In the present communication attempts have been made to establish some suitable conditions of formation, preparation and characterisation of a new heteropoly salt of tantalum with molybdenum as the heteroatom.

Experimental

Solutions of arbitrary concentrations of the reactants may cause immediate precipitation, when they are mixed together, leading to the formation of a compound with indefinite composition. So M/20 molybdic acid and freshly prepared[6] M/50 potassium hexatantalate solutions were found to be workable. The variation of pH changes were recorded against volume[7] when M/20 molybdic acid solution was gradually added into 30 ml of M/50 potassium hexatantalate solution. To corroborate the observation thermometric titrimetric method[7] was also applied. The nature of the graphs are same as reported[7] for 6-heteropoly tantalato tungstate. The pH at which the compound formation is expected in solution phase is around 6. 2, when 30 ml of M/50 potassium hexaniobate solution is mixed with 60 ml, of M/20 molybdic acid. So for the isolation of the compound in solid state, 30 ml of potassium hexaniobate was mixed with 60 ml, solution of M/20 molybdic acid and refluxed

for 4 hrs. in a round bottom flask provided with a series of potash bulb guard tubes which absorbed CO_2 from air. Thus hydrolysis of alkali metal hexatantalate, due to the presence of atmospheric CO_2, was easily avoided. The solution was left for 72 hrs. in vacuum when white powdery compound was separated, filtered, dried and collected. Repeated attempts were made to recover the compound in crystalline form but failed. For analysis of the compound molybdenum was estimated gravimetrically[8] as molybdenum oxinate by 8-hydroxy quinoline method and colorimetrically[9] by potassium thiocyanate method. Tantalum was estimated gravimetrically[10] by precipitating it as tantalic acid with conc. HCl and then weighing as Ta_2O_5 at 850°. Potassium was estimated by flame photometric method and hydrogen was estimated with the help of element estimation technique (Found : Mo, 2.65 ; Ta, 62.07 : K, 8.80 ; H, 1.0 per cent. calcd. for $K_8H_2[MoTa_{12}O_{38}]17H_2O$: Mo, 2.74 ; Ta, 62.14 ; K, 8.95 ; H, 1.03 per cent.). The final representation of the formula was according to the views suggested by Lindqvist[11] for complex heteropoly anion $[X^{n+}Ta_{12}O_{38}]^{(16-n)-}$. According to IUPAC system the compound has been named as heteropoly tantalatomolybdate(VI).

Molecular weight determination—The cryoscopic method, as has been applied successfully by Alexander[12] and by Thilo and Kruger[13] for molecular weight determination of certain inorganic polyacids and polyphosphates, etc., in water and molten sodium sulphate decahydrate ; has also been applied here for the determination of the approximate molecular weight of the compound in the same conditions, i.e., in water and molten sodium sulphate decahydrate[12,13]. This determination showed the molecular weight of the compound to be 3395 as compared with the calculated value 3494.14. As the nature of the compound was amorphous and repeated attempts to isolate a single crystal failed, so the true molecular weight could not be determined by X-ray diffraction technique as has been done in the previous reports[7].

Thermal Depolymerization—The heteropoly acids and their salts can be regarded as condensation inorganic polymers[14]. The thermal depolymerization of the compound has been studied on the light of the investigations made by West and Audrieth[15] on a few heteropoly tungstic acid. The apparatus used for this purpose was that described by Ray and Sinha[16], with continuous pumping the depolymerized product, followed by successive weighing using a thermogravimetric balance and estimations at some stages. The dissociation of the compound was observed at 75° under reduced pressure when six molecules of water were eliminated. At 160° further five molecules of water were lost. The rest of the water molecules remained intact in the crystal latice till 340° above which they were completely removed. When the temperature was raised still higher, then nearly at 720° ± 5°, the compound was broken as a whole into the basic units of lower oxides of molybdenum and tantalum.

Discussion

The X-ray studies of the structure[11] of isopoly unit $[Ta_6O_{19}]^{8-}$ reveals that the six tantalum atoms lie at the centres of six octahedrons while nineteen oxygen atom lie at the apexes forming some sort of projection pattern. Now for the probable configuration of heteropoly unit $[MoTa_{12}O_{38}]^{-10}$, it may be predicted[17] that two isopoly units of $[Ta_6O_{19}]^{8-}$ may condense together and arrange themselves in such a way through oxygen linkage so that there is a vacent space of octahedral size to accomodate one Mo^{+6} ion, which subsequently arrange to give rise : $[MoTa_6O_{19}]^{(-8)+(-8)+(+6)=-10}$. The basicity order has been calculated by considering the ionic charges of each unit, which comes to ten. This agrees with the analytical values on the number of potassium and hydrogen present in the prepared compound $K_8H_2[MoTa_{12}O_{38}]17H_2O$.

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Phenoxide and Naphthoxide Derivatives of Diarylthallium(III) Cation

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THE interaction of dialkylthallium(III) compounds with some substituted phenols is known[1] and a few substituted phenoxide have also been isolated in the crystalline state and characterised[1,2]. In continuation to our studies on diorganothalliums[3-6] now we report the synthesis and characterisation of some diarylthallium(III) phenoxide and naphthoxide (aryl = phenyl, *o*-tolyl *m*-tolyl or *p*-tolyl). The conductometric and I.R. data of the compounds respectively, indicate very feeble ionisation in the solution and a Tl–O bond with insignificant p_π-d_π bonding.

Experimental

Diarylthallium(III) derivatives were prepared according to literature methods[7,8]. Other reagents of analytical grade (BDH/S. Merk) were used without further purification but freshly distilled dimethylformamide was employed in the conductometry.

In a typical preparation, 1 m mole of diarylthallium(III) chloride in 50 ml of pyridine-water mixture (1 : 1) was treated with a concentrated aqueous solution of excess of sodium phenoxide or β-naphthoxide (5 m mole) and the mixture was stirred 4-5 hours on a water bath. The precipitated diarylthallium(III) phenoxide or β-naphthoxide was filtered, washed with water, alcohol and ether and dried at 90° (yield 70-90%). The experimental data are collected in the Table.

The compounds are thermally stable at room temperature but decompose when heated to their melting points. These pale yellow to dirty green crystalline solids are insensitive to atmospheric moisture and oxygen, insoluble in common organic solvents such as benzene, chloroform, diethyl-ether, etc. but dissolve appreciably in pyridine, dimethylformamide and dimethylsulphoxide.

Elemental analyses were done at the Central Drug Research Institute, Lucknow with certain modifications but thallium was estimated as Tl_2CrO_4 from $H_2SO_4-HNO_3$ digested samples[9].

The infrared spectra of the compounds in nujol were recorded in the region of 4000-200 cm^{-1} using Perkin-Elmer spectrophotometer model 521. The calibration was performed with a polystyriene film. The accuracy is thought to be ± 4 cm^{-1}. The melting points of the compounds were determined on electrically operated apparatus, M/s. Toshniwal and Brothers, Bombay, India. Molar conductance of $10^{-3}M$ solutions measured in dimethylformamide using a Phillips conductivity bridge type PR 9500 having a dip type conductivity cell at 30°, was found to be in the range of 2.4-4.3 ohm^{-1} cm^2 mole^{-1} indicating very feeble ionisation of the compounds in solution. Due to insolubility of the compounds in suitable solvents, molecular weight could not be determined either cryoscopically or by the Rast method. This poses restrictions in understanding the degree of polymerisation and to correlate structure with the known compounds.

Various infrared absorptions associated with aromatic group are observed at the positions reported in one of our earlier publications[5], are not listed here. The absorptions associated with asymmetric C–O and symmetric C–O along with Tl–O are summarised in the last column of the Table.

Butcher *et al*[10] examined the spectra of various

TABLE 1—EXPERIMENTAL DATA FOR DIARYLTHALLIUM(III) PHENOXIDE AND NAPHTHOXIDE

Compound	m.p. °C	Analytical data, found (calcd.) % element			I.R absorption bands		
		Tl	C	H	νasym C–O	νsym C–O	νTl–O
$(C_6H_5)_2TlOC_6H_5$	233-34 d	45.4 (45.5)	47.9 (47.8)	3.3 (3.3)	1077 m	1023 s	306 vw
$(o\text{-}CH_3C_6H_4)_2TlOC_6H_5$	210 d	42.7 (42.5)	49.9 (50.1)	4.3 (3.9)	1076 m	1034 m	315 w
$(m\text{-}CH_3C_6H_4)_2TlOC_6H_5$	212 d	42.5 (42.5)	49.9 (50.1)	3.9 (3.9)	1077 w	1025 w	310 w
$(p\text{-}CH_3C_6H_4)_2TlOC_6H_5$	230-33 d	43.0 (42.5)	50.4 (50.1)	4.2 (3.9)	1072 m	1020 m	305 w
$(C_6H_5)_2TlOC_{10}H_7$	210-12 d	40.2 (40.5)	52.2 (52.4)	3.2 (3.3)	1060 m 1070 m	1020 m	312 w
$(o\text{-}CH_3C_6H_4)_2TlOC_{10}H_7$	205 d	38.2 (38.5)	54.6 (54.4)	4.2 (4.0)	–	1030 m	314 m
$(m\text{-}CH_3C_6H_4)_2TlOC_{10}H_7$	208 d	38.5 (38.5)	54.3 (54.4)	4.2 (4.0)	1070 vw	1020 w	308 vw
$(p\text{-}CH_3C_6H_4)_2TlOC_{10}H_7$	240 d	38.0 (38.5)	54.5 (54.4)	4.2 (4.0)	1073 m	1016 s	314 m

d = decomposition, m = medium, s = strong, v = very and w = weak.

*For correspondence

dialkyltin dialkoxides and pointed out that remarkably high intensity of the C – O bands in these compounds is due to $p_\pi - d_\pi$ bonding between the oxygen and tin atoms. The intensity of this absorption in the present investigation is usually weak to medium, which may be due to insignificant $p_\pi - d_\pi$ bonding between the oxygen and thallium atoms on account of the electron withdrawing effect of phenyl and naphthyl group in these compounds. Tl – O stretching vibration in the compounds appears at 310±5 which is close to the reported value for dialkylthallium alkoxides[11].

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Spectrophotometric Determination of Osmium with 2 : 2′-bis (2-pyridyl)-benzothiazole and 2 : 2′-bis(o-mercaptophenyl)-acetylacetonato anil

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Spectrophotometric determination and stability constants of the complexes of osmium with 2 : 2′-bis(2-pyridyl)-benzothiazole (Reagent I) and 2 : 2′-bis(*o*-mercaptophenyl)-acetylacetonato anil (Reagent II) respectively, have been made. The maximal absorption being 490 nm and 480 nm for reagents I and II, at 0.50 to 3.0*M* and 0.10 to 2.0*M* HCl medium, whereas sensitivities are 0.0200μ g cm^{-2} and 0.0250μ g cm^{-2} respectively. The optimal ranges for Beer's law are 4 to 16 ppm and 4 to 12 ppm for reagents I and II, the per cent. relative analysis errors being 2.60 and 2.74 respectively, whereas molar extinction coefficient values are 1.0×10^4 mole cm^{-1} and 7.25×10^3 mole cm^{-1}. Composition of the complexes are evaluated and stability constants were calculated by the Leden's and Rosenstein's methods, which agree quite well.

Organic reagents having N, O or S donor atoms have been described for spectrophotometric determination of osmium[1-3]. They offer varied nature of sensitivity and selectivity under experimental conditions. Chelating agents containing C – S bridge or S – S bridge have a tendency to give coloured complexes with osmium. Sulphur can take part in M→L back π-bonding causing therein high stability. In this present paper, spectrophotometric determination of osmium and evaluation of stability constants have been described with reagents like benzothiazole containing C – S bridge and a Schiff's base anil containing S – S bridge. Both the reagents give red or red-violet coloured complexes with osmium and are suitable for spectrophotometric determination. The systems of osmium complexes are sensitive, follow Beer's law over a considerable range. The stability constants of the complexes were evaluated by a few standard methods where they agree quite well.

Reagents, Apparatus and Solutions

Preparation of 2 : 2′-bis(2-pyridyl)-benzothiazole [Reagent-I]

2 : 2′-bis pyridyl ketone (A.R. grade) and 2-amino thiophenol (Fluka) in 1 : 1 mole ratio was refluxed in absolute alcohol for 6 hours. The reaction mixture on cooling gave pale yellow crystals. The product was recrystallised from absolute ethanol to give white needle-shaped crystals. Yield—40% m.p. 132°. On analysis : found, 69.79% C, 4.36% H, and 14.30% N, Calc. for $C_{17}H_{13}N_3S$, 70.00% C, 4.47% H and 14.43% N.

2 : 2′-bis-(*o*-mercaptophenyl)-acetyl acetonato anil (a Schiff's base) [Reagent-II].

Acetyl acetone (BDH) 10 g and 2-amino-thiophenol (Fluka) 25 g were refluxed in benzene medium in presence of 25 ml of freshly distilled pyridine for 6 hours when a deep orange mixture was obtained. On cooling at room temperature for 2 days, orange crystalls separated out which was washed with ligroin and dried in vacuum.

Yield—2.5 g ; m.p. 184°

Analysis : found, 64.27% C, 5.61% H and 8.49% N Calc. for $C_{17}H_{18}N_2S_2$, 64.97% C, 5.76% H and 8.91% N.

A Hilger uvispek spectrophotometer using 1 cm glass or quartz cells was used for measurements of absorptions.

Standard osmium(VIII) solution was prepared as suggested by Ayres and Wells[3] and standardized[4] iodometrically.

Standard solution of hydrochloric acid and of diverse ions were prepared from A.R. grade reagent and determined by standard methods.

Reagent solutions

Solutions of the reagents 0.2% w/v and 0.1% w/v were prepared in 95% ethanol for reagents I and II respectively.

Coloured complexes were obtained by adding ethanolic solutions of reagents to osmium(VIII) solution. Since, osmium(VIII) is reduced to osmium(VI) with ethanol used as a solvent for reagent solution, the colour reactions are actually with osmium(VI) ions.

Absorption spectra

Absorbances of the complex with Reagent-I containing 6 ppm of osmium and 2.5 ml of 0.2% (w/v) reagent solution at 2 *M* HCl concentration were measured against reagent blank from 400 to 675 nm and maximal absorbance was found to be at 490 nm, whereas absorbance of the reagent in that region is very low. With Reagent-II absorbances were measured of a solution containing 5 ppm of osmium and 4 ml of 0.1% (w/v) reagent solution at 1 *M* HCl concentration from 420 to 600 nm. The absorbances of the reagent continuously decreased and at 470 nm and above had no absorption while maximal absorption of the complex was at 480 nm.

Effect of variables

With Reagent-I maximal colour intensity was found to be in 0.50 to 3.0 *M* hydrochloric acid medium. With 4 ppm of osmium 0.4 ml of 0.2% (w/v) reagent solution was found to be sufficient for complete colour development. With the same amount of osmium, up to 4.0 ml of 0.2% (w/v) reagent solution had no adverse effect on absorbance values. With Reagent-II, maximal absorption was found in 0.10 to 2.0 *M* HCl concentration. With 5 ppm of osmium 1 mole of 0.1% (w/v) reagent solution was found to be sufficient for complete colour development and with same amount of metal up to 5.0 ml of 0.2% (w/v) reagent solution did no effect the absorption of the complex system. The complexes are stable for 3 and 2 hours with Reagents I and II respectively. In both the cases, ethanol up to 70% concentration used as solvent in reagent solutions had no adverse effect on the absorption systems. Spectral studies were made at room temperature 27±2°.

Recommended procedure

Reagent-I

In a 25 ml. volumetric flask, take 1.5 ml of osmium(VIII) solution containing 0.1 mg and add 2.5 ml of 0.2% (w/v) reagent solution followed by 10 ml of 5 *M* hydrochloric acid solution and make up the volume with double distilled water. Measure the absorbance value against a reagent blank.

Reagent-II

In a 25 ml volumetric flask, take 1.25 ml of osmium(VIII) solution having 0.1 mg/ml and add 4 ml of 0.1% (w/v) reagent solution. After 5 min. an amber colour developed. And 5 ml of 5 *M* hydrochloric acid solution and make up the volume and measure absorbance as usual.

Beer's law

The complex system with Reagent I obeys Beer's law from 1 to 16 ppm of osmium, the optimal[5] range being 4 to 16 ppm. Sensitivity[6] and % relative analysis error[7] being 0.0200μ g cm^{-2} and 2.60, respectively. With Reagent II Beer's law is obeyed from 2 to 16 ppm of osmium, optimal range being 4 to 12 ppm. Sensitivity and % relative analysis error being 0.0250 μ g cm^{-2} and 2.74 respectively. The molar extinction coefficients of the complexes with Reagents I and II, evaluated by extrapolation are found to be 1.0 x 10^4 mole cm^{-1} at 490 nm and 7.25 x 10^3 mole cm^{-1} at 480 respectively.

Composition of the complexes

Compositions of the complexes with Reagents I and II were determined by Job's method[8] of continuous variation and were confirmed by molar ratio method[9]. In both the cases, Job's method indicated that osmium and reagent are in the ratio of 1 : 1 and mole ratio method confirmed this finding.

Effect of diverse ions

To find out the effect of diverse ions on the complex system, solutions containing a definite amount of osmium(VIII) but varying amounts of foreign ions were prepared and absorbances were measured. A deviation of 0.005 unit of absorbance value from the original was considered as interference. Of the tested cations and anions, with 4 ppm of osmium(VIII) following ions did not interfere in ppm unit.

Reagent-I	Reagent-II
Mn(II)-200, Cu(II)-100	Mn(II)-100, Co(II)-50
Ru(III)-200, Ir(III)-400	Ru(III)-100, Ir(III)-400
Fe(III)-50, Co(III)-100	Pt(II)-50
PO_4^{-3}-400, Citrate-100	PO_4^{-3}-400, Borate-200
HF_2^--200, Borate-100	
Tartrate-200, SCN^--200	
NO_3^--200	

With Reagent-I, ions like Pt(II), Pd(II), Ni(II), V(V) and oxalate interfere.

With Reagent-II, Pd(II), Cu(II), Fe(III), V(V), Ni(II), SCN^-, Citrate, Tartrate, HF_2^- however interfered the complex system.

However, to overcome interference due to cations, there are recommended procedures[10] by a prior distillation of Os(VIII) in HNO_3 medium as OsO_4.

Degree of dissociation, dissociation constant and stability constant

Using the equation of Harvey and Manning[11], the degree of dissociation and dissociation constant were calculated and found to be 0.184 and 1.79×10^{-6} for Reagent-I and 0.159 and 1.27×10^{-6} for Reagent II respectively.

Stability constants were calculated[12,13] from molar ratio data according to Leden's method[16]. Using the following equation: $\phi=1+\beta_1[L]+\beta_2[L]^2+\ldots+\beta_n[L]^n$, where $\phi=\frac{CM}{[M]}$ for the equation $M+nL=ML_n$. The value of the function. ψ_1 is obtained from the equation[14],

$$\psi_1=\frac{\phi-1}{[L]}=\beta_1+\beta_2[L]+\ldots\ldots\ldots\ldots \text{ for } 1:1\ (M:L)$$

systems $\psi_1=\beta_1$.

Stability constants were also evaluated by Rosenstein's method[15].

For 1 : 1 metal-ligand system at an wave length where metal and reagent have no or negligible absorbance, i.e.,

$$\epsilon_o=\epsilon_L=0,$$

$$M+L \overset{\beta_1}{\rightleftharpoons} ML, \text{ stability constant } \beta_1 \text{ is given by}$$

$$\frac{\bar{\epsilon}}{\epsilon_1-\bar{\epsilon}}=\beta_1[L]$$

In both the cases notations have their usual significance. β_1 was evaluated graphically in both the cases and found as follows:

Stability constant calculated by,—	Reagent-I	Reagent-II
(i) Leden's method	1.3×10^5	0.90×10^5
(ii) Rosenstein's method	2.5×10^5	2.0×10^5
Mean β_1	1.9×10^5	1.45×10^5

Results and Discussion

The benzothiazole reagent could satisfactorily be used for spectrophotometric determination of osmium with limited interference and is suitable for routine laboratory analysis. The Schiff's base anil reagent though cannot tolerate a number of foreign ions in the system, it is the first one of a series of di-anils. Other reagents which have already been utilised by the authors, where $-CH_3$ groups of the diketones have been replaced by other radicals to give more sensitive and selective reagents for determination of osmium. These reagent are not only restricted for use to osmium only but could be extended to the field of other platinum metals, such as Pt and Pd. Such studies are in progress in this laboratory. The authors have already prepared three more reagents by condensing benzoylacetone, dibenzoyl methane and thenoyl trifluoro acetone with 2-aminothiophenol and their studies on osmium and other platinum metals will be reported shortly.

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A New Method for the Geochemical Exploration of Trace Amount of Barium and Strontium Using SPADNS

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In view of the need for a rapid method of the determination of trace amount of Ba and Sr, a direct colorimetric method has been developed using SPADNS[1-4] for the micro-determination of barium as little as 0.2μ g and of strontium as little

as 0.3μg in 25 ml of final volume with the adjustment of pH using ammonium chloride-ammonia buffer and dil. HCl or dil. NH_4OH.

The method is advantageous because of easy preparation of the reagent, marked colour change from scarlet-red to blue-violet, immediate colour reaction, stability of the reagent and low temperature coefficient.

Experimental

The Ba-SPADNS complex and the Sr-SPADNS complex show maximum absorbance at 570 nm and 560 nm respectively using distilled water as a reference. The absorption maxima of the reagent against water for barium and strontium are 522 nm and 520 nm respectively.

The effect of pH on the absorbance was studied. The maximum absorbance was noticed at pH 10-11 for Ba and pH 8.5-9.5 for Sr respectively. Ammonium chloride-ammonia buffer, dil. HCl or dil. NH_4OH were used for varying pH. The Beer's law is obeyed in the range 0.2-60 μ g of Ba and 0.3-60 μ g of Sr respectively. The molar absorptivities of Ba-SPADNS and Sr-SPADNS are 1.3×10^4 (at 570 nm) and 4.3×10^3 (at 560 nm) respectively. No change in optical density was noted for 72 hours for Ba-SPADNS and 4 hours for Sr-SPADNS complexes which suggests that they are sufficiently stable for quantitative determinations.

The sensitivities of the colour reactions are 0.2μg Ba per cm^2 and 0.3μg Sr per cm^2 (practical) respectively. The stoichiometric composition of the coloured complexes have been determined colorimetrically by adopting the "Slope Ratio Method" and "Job's method"[5,6] which suggest a 1 : 1 complex for both the elements with the reagent. Nearly all the elements associated with Ba and Sr were tested to determine the behaviour with SPADNS under the optimum conditions used for Ba-SPADNS and Sr-SPADNS reactions. It has been found that 10 mg amounts of Zn, Fe, Cu, Pb, Ni, V, Nb, Sb, As, Cr, Ga, Ir, Sn, Au, Ag and W do not interfere in the determination of these elements. However, Ca. Mg and Ba in presence of Sr and Sr in presence of Ba interfere seriously.

As the absorption maxima of Ba and Sr are very close to each other, these elements can't be determined by simultaneous spectrophotometry.

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Kinetic Study of Oxidation of Aliphatic Dicarboxylic Acids by Cerium(IV) Ion in Acidic Medium

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A review of the literature shows that the oxidation of aliphatic dicarboxylic acids by cerium(IV) ion has not received much attention. Only recently a preliminary work[1-4] on the oxidation of oxalic acid, malonic acid has been carried out but the mode of attack of the acids by oxidation species from the Ce(IV) ion has not been worked out, nor the different stages involved, and the effect of $-CH_2$ group on the overall reaction rate in the process elucidated. Hence, we have undertaken a systematic kinetic study of the oxidation of aliphatic dicarboxylic acids—oxalic, malonic, succinic and glutaric acid by ceric sulphate in acidic medium. Comparative kinetic data of these studies is present in this paper which has enabled us to arrive at a suitable reaction mechanism and the effect of $-CH_2$ group for this class of reactions.

Experimental

All the chemicals used were either 'Analar or E.Mercks' guarenteed reagent quality. The stock solution of ceric sulphate was prepared by dissolving a known amount of it in calculated volume of sulphuric acid and diluting with double distilled water. The solutions of the reactive substances were brought to the required temperature in a thermostat, which maintained the temperature at a constant value with in $\pm 0.1°$ and then rapidly mixed. Aliquots were withdrawn at known intervals of time and reaction was stopped by adding ice-cold double distilled water. The estimation of unreacted ceric(IV) was done with standard solution of ferrous ammonium sulphate solution using ferroin as an indicator.

Results

All these reactions have been found to show pseudo first order w.r.t. ceric sulphate. However, the pseudo first order rate constant generally

decreases slightly with time in any particular kinetic run. The rate of reaction in each case is also pseudo first order w.r.t. organic acid. It increases with an increase in the concentration of organic acid.

The pseudo first order behaviour of the reaction w.r.t. organic acid in each case has been confirmed by plotting 1/K vs. 1/[Reductant]. The plot for each acid is a straight line which does not pass through the origin but cuts 1/K axis at a certain distance, giving as information about the complex formation between cerium(IV) and organic acid which is in the confirmity with the mechanism postulated by us.

The rate of reaction in each case is inversely proportional to the square of the concentration of sulphuric acid. The plot of K vs. $1/[H_2SO_4]^2$ is a straight line in each case. This fact is confirmed by mechanism elucidated. The similar behaviour has been reported by Krishna and Tiwari[5] in the oxidation of hydroxy acid by Ce(IV) ion.

The mole ratio of ceric sulphate is 2 : 1, 6 : 1, 10 : 1 and 14 : 1 with oxalic acid, malonic, succinic, and glutaric acids respectively. It is obvious that with an increase of one $-CH_2$ group in the acid, the 4 moles of ceric sulphate are more needed for the oxidation of organic acid. The overall reaction on the basis of stoichiometry may be written as below for different acids.

It is clear from the above data that the free energy of activation is of similar order of magnitude in the four cases ; the energy of activation is nearly the same in all reactions except in the case of malonic acid. The value of $\Delta S^{\neq}$ is large and negative and frequency factor[6] in each case is of the order less than 10^{10} sec^{-1}, suggests the chain mechanism involving free radical in all these four reactions.

Discussion

The final products of oxidation of malonic, succinic and glutaric acid are formic acid and CO_2, while oxalic acid is oxidised into water and CO_2. The formation of the products is through the complex formation between Ce(IV) and the concerned acid. The complex being unstable decomposes into acid aldehydes and Ce(III). The acid aldehydes so formed are oxidised by Ce(IV) to formic acid and CO_2 as is seen in the case of malonic acid[7] oxidation by Ce(IV) and malic acid oxidation by quinquivalent vanadium[8].

The general rate expression for this class of compounds by Ce(IV) adopting the mechanism of Hardwick and Robertson[9] has been derived as :

$$\frac{-d[Ce(IV)]}{dt} = k.\ [Ce(IV)]$$

which in the velocity equation obtained experimentally by us.

$$\begin{array}{l} COOH \\ | \\ COOH \end{array} + 2Ce(IV) \longrightarrow 2Ce(III) + 2H^+ + 2CO_2 \quad \ldots\ldots \quad (a)$$

$$CH_2\begin{array}{l} \diagup COOH \\ \diagdown COOH \end{array} + 6Ce(IV) + 2H_2O \longrightarrow 6Ce(III) + 6H^+ + HCOOH + 2CO_2 \quad \ldots\ldots \quad (b)$$

$$\begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \end{array} + 10Ce(IV) + 4H_2O \longrightarrow 10Ce(III) + 10H^+ + 2HCOOH + 2CO_2 \quad \ldots\ldots \quad (c)$$

$$CH_2\begin{array}{l} \diagup CH_2COOH \\ \diagdown CH_2COOH \end{array} + 14Ce(IV) + 6H_2O \longrightarrow 14Ce(III) + 14H^+ + 3HCOOH + 2CO_2 \quad \ldots\ldots \quad (d)$$

Energy Parameters

The various energy parameter of these reaction are recorded together in Table 1.

TABLE—1

Reductant Acid	Energy of activation (E) in K cals.mole^{-1}	Entropy of activation ($\Delta S^{\neq}$) E.U.	Free energy ($\Delta G^{\neq}$) in K cals.mole^{-1}
Oxalic	12.6	−35.4	22.4
Malonic	10.8	−41.8	22.3
Succinic	13.9	−37.6	25.5
Glutaric	12.4	−41.6	25.3

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Estimation of Crotyl and Cinnamyl Alcohols with Dichloramine-T in Partially Aqueous and Non-aqueous Media

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ORGANIC haloamines have found increasing applications as mild oxidants and analytical reagents in the estimation of compounds in solution. Dichloramine-T (N, N'-dichloro-*p*-toluene sulphonamide, hereinafter abbreviated as DCT) has been introduced by Jacob and Nair[1] as an oxidimetric reagent in non-aqueous and partially aqueous media and it has been used for estimating a variety of compounds such as hydroquinone[2], oxine[3], metal oxinates[3], thiols and their metal complexes[4,5], metal cyanides and their complexes[6] and indigocarmine and isatin[7]. Conjugated alcohols such as crotyl alcohol and cinnamyl alcohol have a number of important applications. Crotyl alcohol finds use as a lachrymator, herbicide and soil fumigant, while cinnamyl alcohol is employed as a flavouring agent and in perfumery. In the present investigations, we have examined the behaviour of DCT towards these alcohols. While the oxidation of alcohols was found to be sluggish in 50% v/v ethanol medium, crotyl alcohol in partially aqueous medium and cinnamic alcohol solution in glacial acetic acid could be oxidized by DCT, with a two electron change. The rate was not rapid enough for a direct titration of alcohols with visual or potentiometric end point detection and hence back titration procedures were employed.

Experimental

Crotyl alcohol (Fluka, B.P. 125°, $n_D = 1.424$) was used without further purification, but the purity was checked by phthalation with phthalic anhydride in pyridine[8]. Aqueous solutions containing a definite weight of the alcohol were prepared. Cinnamyl alcohol (Naarden, corrected B.P. 256.6°) was distilled under reduced pressure and the purity was checked[9]. Solutions of the compound in glacial acetic acid were prepared by dissolving weighed amounts of the sample.

Dichloramine-T was prepared and purified by the method of Jacob and Nair[1]. An approximately decinormal solution of the oxidant in glacial acetic acid (containing 10% v/v acetic anhydride) was prepared and standardized by the iodometric method[1].

Preliminary Studies :

Known volumes of alcohol solution were added to a known excess of decinormal DCT solution in an iodine flask. The reaction mixture was kept at room temperature with occasional shaking, for different intervals of time. About 10 ml of 20% KI solution were then added and the liberated iodine was titrated against sodium thiosulphate solution. A blank titration was carried out with the same volume of DCT. The time required for the stoichiometric oxidation of crotyl and cinnamic alcohols by DCT was calculated. Table 1 shows the extent of oxidation of the alcohols with DCT. It is seen that stoichiometric oxidation of crotyl alcohol with a two electron change takes place in about 45 minutes while cinnamic alcohol requires 90 minutes in the concentration range used.

TABLE 1—EXTENT OF OXIDATION OF CROTYL AND CINNAMIC ALCOHOLS WITH DICHLORAMINE-T

Time (minutes)	Equivalents of DCT consumed × 10³	Equivalents of DCT consumed / Equivalents of alcohol taken
	Crotyl alcohol	
5	0.2951	1.77
10	0.3165	1.89
20	0.3272	1.96
30	0.3307	1.98
45	0.3343	2.00
60	0.3343	2.00
18 hrs.	0.3360	2.01
	Cinnamic alcohol	
10	0.1340	1.11
20	0.1952	1.61
30	0.2105	1.74
45	0.2258	1.87
60	0.2325	1.93
70	0.2343	1.95
90	0.2418	2.00
120	0.2418	2.00
16 hrs.	0.2433	2.01

Crotyl alcohol taken : 0.1671 m mole.
DCT taken : 0.25 m mole.
Cinnamic alcohol taken : 0.1211 m mole.
DCT taken : 0.41 m mole.

Recommended Procedure :

An aliquot of alcohol solution (2-36 mg) was added to a known excess of DCT (~ 0.40 m mole) in an iodine flask at room temperature (25±2°). The reaction mixture was shaken and kept aside for 45 and 90 minutes respectively for crotyl and cinnamic

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alcohols. The unconsumed DCT was estimated by adding 10 ml of 20% KI and titrating the liberated iodine against standard sodium thiosulphate using starch as internal indicator. A blank titration was run with the same volume of DCT.

Results and Discussion

The stoichiometry of the oxidation of alcohols with DCT can be represented by equations (1) and (2).

$$CH_3CH=CHCH_2OH+\frac{1}{2}RNCl_2 \rightarrow CH_3CH=CHCHO+\frac{1}{2}RNH_2+HCl \quad \ldots\ldots(1)$$

$$C_6H_5CH=CHCH_2OH+\frac{1}{2}RNCl_2 \rightarrow C_6H_5CH=CHCHO+\frac{1}{2}RNH_2+HCl \quad \ldots\ldots(2)$$

The presence of crotyl and cinnamyl aldehydes in the reaction mixture was shown by spot tests[9]. Further, the aldehydes were isolated as their 2,4-dinitrophenyl hydrazone[10] (M.P. 189° and 253° respectively for the hydrazones of crotyl and cinnamyl aldehydes). The sulphonamide was identified by TLC technique[11]. The solvent was a mixture of chloroform, ethanol and heptane (1 : 1 : 1 by volume) and *p*-dimethyl amino benzaldehyde in 2 NHCl was used as the spray reagent (R_F = 0.93).

Some typical results of analyses are given in Table 2. The maximum deviation observed in recovery is about 0.7%. The effect of water on the stoichiometry of oxidation of alcohols by DCT was studied. While it had little influence on the oxidation of crotyl alcohol by DCT, recoveries of cinnamyl alcohol were 3% higher when water is present above 8% in the reaction mixture. The presence of neutral compounds on the rate of oxidation of alcohols by DCT was investigated. It was seen that KCN, KCNS, NaCl (~ 0.94 m mole), KBr and KI interfere in the estimation, while Na_2HPO_4 and $ZnSO_4$ had no influence.

TABLE 2—ESTIMATION OF CROTYL AND CINNAMYL ALCOHOLS WITH DICHLORAMINE-T

Crotyl alcohol			Cinnamyl alcohol		
Compound taken mg	Compound found mg	Per cent. deviation	Compound taken mg	Compound found mg	Per cent. deviation
6.03	6.05	+0.33	2.20	2.21	+0.45
9.05	9.07	+0.22	4.50	4.53	+0.67
12.05	12.06	+0.083	6.70	6.72	+0.30
15.08	15.10	+0.13	8.90	8.93	+0.34
18.10	18.13	+0.17	11.10	11.15	+0.45
24.20	24.30	+0.41	13.40	13.45	+0.37
30.10	29.90	−0.66	17.80	17.88	+0.45
36.10	35.90	−0.55	22.30	22.40	+0.45

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Study of Essential Oil of *Cymbopogon nardus* var. *stracheyi*

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CYMBOPOGON nardus var. *stracheyi* (N. O. Graminae), a medicinal-aromatic species, possesses high content of the essential oil. The oil has been found to possess antibacterial and antifungal properties[1]. Orange coloured essential oil from the fresh plant material was extracted by water-steam distillation in 0.25% yield. The physicochemical properties determined by usual methods[2] were: specific gravity = 0.8924/20°, refractive index = 1.4824/20°, specific rotation = +2°/20°, acid value = 0.68, ester value = 18.75, ester value after acetylation = 98.39 and carbonyl value as $C_{10}H_{16}O$ (oximation, potentiometry) = 8.2.

The oil (100 ml) was fractionated into its constituents employing (i) fractional distillation under reduced pressure (3-4 mm), (ii) column chromatography—using neutral alumina as adsorbent and petroleum ether, *n*-hexane, cyclohexane, benzene, ether, ethyl acetate as eluents. The purity of each fraction was ascertained by thin-layer chromatography and gas-liquid chromatography. In all ten pure fractions were obtained which were identified by preparing their characteristic derivatives and comparing their properties to those mentioned in literature[3]. The presence of β-pinene, l-limonene,

methyl heptenone, *d*-α-phellandrene, *d*-citronellal, linalool, citronellol, nerol, geraniol and geranyl acetate was established.

The I.R. spectra and co-TLC of the fractions also confirmed the above results. The alcohols were confirmed by the TLC of their 3,5-dinitrobenzoates over Silica Gel G coated glass plates using different solvent systems and anisaldehyde-H_2SO_4 as spray reagent. The R_B values (using butter yellow as a reference compound) in benzene-petroleum ether (1 : 1) were observed to be 1.6, 1.3, 1.2 corresponding to citronellol, nerol and geraniol respectively.

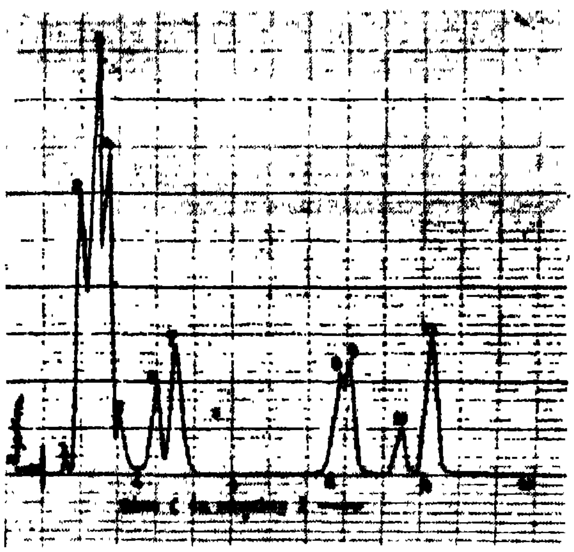


Fig. 1.

Chromatogram : Oil of *Cymbopogon nardus* var : stracheyi

Conditions—
Column—10% Carbowax 20 m
Column temp.—180°C
Carrier gas—Hydrogen (40 ml/min)
Chart speed—0.25 inch/min.

Gas-liquid Chromatography : The GLC of the oil was carried out in a gas chromatograph model—Honeywell HP 7620A equipped with thermal conductivity detector and Carbowax 20*M*, 10% (18 ft.) column. The column and injection port temperatures were maintained at 180° and 200° respectively, and hydrogen (40 ml/min.) was used as carrier gas. The eleven peaks obtained in the chromatogram were identified by comparing their retention and relative retention times to those of the authentic samples recorded under identical operating conditions. The percentage of each constituent in the oil was determined by calculating corresponding peak area by height × width at half height method. The results are summarised in Table 1.

Thus, the GLC revealed the presence of one more constituent, i.e., camphene in addition to those identified by chemical methods.

TABLE 1—GLC OF ESSENTIAL OIL OF *C. nardus* VAR. *stracheyi*

Peak No.	Retention time (minutes)	Percentage in the oil	Compound
1	1.3	0.25	camphene
2	1.5	15.0	β-pinene
3	2.0	28.0	limonene
4	2.5	16.25	α-phellandrene
5	3.0	3.0	methyl heptenone
6	4.6	5.5	citronellal
7	5.6	8.0	linalool
8	12.6	6.0	citronellol
9	12.7	7.0	geranyl acetate
10	14.8	3.0	nerol
11	16.2	8.0	geraniol

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Colouring Matters from the Flowers of *Thunbergia laurifolia*

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THE plant *Thunbergia laurifolia* (N. O. Acanthaceae) is a large climber and is found throughout India[1]. The flowers, light blue in colour with yellowish throat, on chemical examination yielded Delphinidin 3 : 5-di-o-β-D-glucopyranoside, apigenin and apigenin-7-o-β-D-glucopyranoside.

The fresh flowers were extracted with 1% methanolic hydrochloric acid and the extract after concentration under reduced pressure was extracted with ether. The violet red solution gave compound A and the dried ether extract on crystallisation from acetone : methanol (1 : 1) gave compound B. The extracted flowers were air-dried and refluxed with ethanol for 10 hr. The concentrated extract on crystallisation from methanol : benzene (1 : 1) gave compound C.

Compound A (*anthocyanin*) ; violet-red ; hygroscopic ; λ_{max} 535 nm, shift in $AlCl_3$ (25 nm). Hydrolysis with 20% $CH_3OH-HCl$ gave anthocyanidin and a sugar identified to be D-glucose. The antho-

cyanidin was identified to be Delphinidin by its standard R_f values[2], colour reactions[3] and λ_{max} 545 nm, shift in $AlCl_3$(25 nm). Periodate oxidation and the hydrolysis with emulsin suggested the glucose molecules to be in pyranose forms and linked through β-linkages. The anthocyanin was confirmed by direct comparison with its authentic sample isolated from *Verbena hybrida*[4].

Compound B (*flavone aglycone*); yellow solid. $C_{15}H_{10}O_5$, m.p. 346°, gave negative Molisch test; λ_{max} 269 nm and 336 nm; R_f value 0.88 in *n*-butanol : acetic acid : water (4 : 1 : 5); $KMnO_4$ oxidation gave *p*-hydroxy benzoic acid and KOH fusion gave phloroglucinol indicating the presence of free hydroxyls at positions-4', 5 and 7. These positions were also shown by the colours given with $NaHCO_3$ (blue), methanolic ZrOCl (yellow) and vanillin – HCl reagent (pink) and confirmed by the bathochromic shifts with $NaOC_2H_5$(56 nm in Band I), $AlCl_3$(9 & 46 nm) and fused NaOAc (9 & 40 nm). Hence, the compound B was identified to be a 4', 5 : 7 trihydroxy flavone, i.e., apigenin.

Compound C (*flavone glycoside*); yellow crystals; $C_{21}H_{20}O_{10}$; m.p., 174°; gave positive Molisch test showing its glycosidic nature; λ_{max} 268 nm and 335 nm. Hydrolysis with 10% H_2SO_4 gave an aglycone identical to the compound B and a sugar identified to be D-glucose. Oxidation with $KMnO_4$ gave *p*-hydroxy benzoic acid. The negative colour test with vanillin-HCl reagent and no shift in Band II with fused NaOAc indicated the position-7 to be glycosylated.

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Flavonoids from Flowers of *Hamellia patensa*

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HAMELLIA patensa (N.O. Rubiaceae) is a shrub of immense medicinal use, Presence of two authocyanins viz. Petunidine 3,5-diglucoside and Malvidine 3,5-diglucoside have already been reported from the fresh flowers[1]. In the present communication the authors wish to report the flavonoidal constituents of the flowers of H. patensa.

The air dried flowers (about 2 Kg.) of H. patensa were extracted with acetone under reflux on a steam bath. The acetone extract was concentrated to a syrapy mass and was poured in large excess of water. The water soluble and water insoluble fractions were separated. The water soluble fraction was concentrated and successively subjected to sexhelet extraction with petroleum ether, benzene and ethyl acetate. The ethyl acetate fraction was concentrated and then adsorbed over a column of magnesol. Elution with ethyl acetate yielded two substances A and B. Both these substances gave positive Molisch's test. The purity of the substances was checked by P.C. and T.L.C.

The compound A crystallised from acetone M.P. 340-2° (d) $C_{21}H_{18}O_{11}$ when being hydrolysed yielded an aglycone M.P. 349-50° $C_{15}H_{10}O_5$ which gave positive colour reactions (e.g., Mg/HCl) for flavonoids and was found to be identical with apigenin (M.P. U.V. shift, Co. chromatography, m.m.p. and super imposable I.R. spectra with authentic sample), and glucuronic acid as Sugar moity (identified by paper chromatography with authentic sample). Compound A was thus characterised as Apigenin-7-glucuronide[2].

The compound B Crystallised from Methanol M.P. 188° $C_{27}H_{30}O_{16}$. On acid hydrolysis yielded an aglycone M.P. 316°, $C_{15}H_{10}O_7$ identical with quercetin (by m.m.p. and co-chromatography with authentised sample) and sugars D(+) glucose and L(–) rhamnose (identified by paper chromatography with authentic sample). Hence compound B was identified as rutin[3] by m.m.p. chromatography and super imposable I.R. spectra with authentic sample.

The water insoluble fraction of the acetone extract was chromatographed on a column of magnesol which was eluted with ethyl acetate. The eluate yielded compound C which responded positive test for flavones. It was recrystallised from acetone-methanol (3 : 1 V/V) m.p. 348-50° $C_{15}H_{10}O_5$. It did not respond to Molischi's test. It was identified as apigenin by m.m.p., super imposable I.R. and co-chromatography with authentic sample.

Acknowledgement

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Studies on the Suppression of Polarographic Maximum of Nitrobenzene by Ionic and Non-ionic Surfactants vis-a-vis their Influence on the Kinetics of the Electrode Reaction

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LAL and Srivastava[1] have studied the suppression of polarographic maximum of nitrobenzene by some ionic and non-ionic surfactants with a view to compare their relative efficacies for quenching the maximum to half of the original value. In the present paper an attempt has been made to study the kinetics of the electrode reaction of nitrobenzene as a function of concentration of some more ionic and non-ionic surfactants from the stage where maximum just disappears. This provides a better opportunity for comparing the efficacy of different surfactants in suppressing the maximum.

Experimental

All the chemical used were of BDH Analar grade. The surfactants used were: Lauryl pyridinium chloride (LPC), Cetyl pyridinium chloride (CPC), Cetyl dimethylbenzylammonium chloride (CDBAC), Sodium lauryl sulphate (SLS), Dodecylbenzene sulphonate (DBS), Dioctyl sodium sulphosuccinate (DSSS), Triton X-100, 2-ethoxy ethanol, Ethyldigol and Gelatin.

A manual polarograph (Toshniwal, CLO2) in conjunction with a polyflex galvanometer (Toshniwal, PL50) was used. All the measurements were made at 25±0.1° using McIlvaine buffer (*p*H 7). The purified nitrogen was used for removing the dissolved oxygen. The potentials were measured against a saturated calomel electrode (S.C.E.). The d.m.e. had the following characteristics (in 0.1 *M* KCl, open circuit).

$h_{corr} = 73.12$ cm ; $t = 3.60$ sec ;
$m^{2/3}t^{1/6} = 2.672$ mg$^{2/3}$sec$^{-1/2}$

The number of electrons (n) involved in the reduction process was determined by millicoulometric method of Devries and Kroon[2] using a mercury pool cathode. This gave the value of n equal to 4 at *p*H 7. Having known the value of n, Ilkovic equation was used to calculate the value of D, the diffusion coefficient of nitrobenzene at various concentrations of the surfactants.

Results and Discussion

Nitrobenzene under the chosen experimental conditions yields a negative maximum at −0.70V (S.C.E.). The values of polarographic characteristics of nitrobenzene in the presence of minimum amount of each surfactant needed to suppress the maximum have been summarised in Table 1. Representative Fig. 1. depicts the effect of increasing amounts of LPC on current-voltage curves. After the removal of the maximum the limiting current has been found to be diffusion controlled in each case as evidenced by the linearity of i_d vs $\sqrt{h}$ plots.

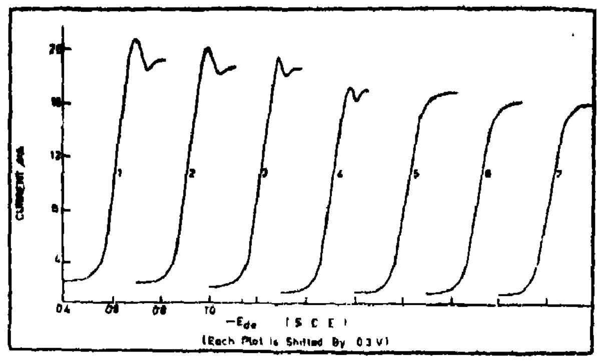


Fig. 1 C−V curves of Nitrobenzene in the presence of different concentrations of LPC.
[LPC] 1. 0.0%, 2. 8.0×10^{-11}%, 3. 1.6×10^{-10}%, 4. 2.4×10^{-10}%, 5. 3.2×10^{-10}%, 6. 4.0×10^{-10}%, 7. 8.0×10^{-10}%.

On applying various tests of irreversibility[3-6] it has been found that the reduction of nitrobenzene at d.m.e. is totally irreversible. The potential dependent rate constant ($k_{f,h}$) for the electrode reaction has been calculated by Koutecky's method[7]. Having calculated $k_{f,h}$ at various stages of a wave αn_a values were calculated from the slope of log $k_{f,h}$ vs $E_{d.e.}$ plots[8] and are listed in Table 1.

TABLE 1.—POLAROGRAPHIC CHARACTERISTICS OF NITROBENZENE (25% ETHANOLIC SOLUTION) IN McILVAINE BUFFER (*p*H 7)
[Nitrobenzene] = $1.0\times10^{-3}M$

Surfactant used	i_d μA	$-E_{1/2}$ V S.C.E.	Slope mV	αn_a
Cationic				
LPC (3.2×10^{-10}%)	14.72	0.62	68	0.76
CPC (2.8×10^{-10}%)	14.82	0.63	71	0.81
CDBAC (1.2×10^{-10}%)	15.25	0.60	59	0.92
Anionic				
SLS (3.2×10^{-10}%)	15.96	0.64	74	0.73
DBS (1.6×10^{-10}%)	14.01	0.62	69	0.78
DSSS (2.4×10^{-10}%)	14.72	0.64	76	0.72
Non-ionic				
Gelatin (4.0×10^{-8}%)	16.32	0.60	100	0.60
Triton X-100 (1.6×10^{-8}%)	15.08	0.62	68	0.78
2-Ethoxy ethanol (1.6×10^{-6}%)	16.85	0.62	84	0.73
Ethyldigol (1.6×10^{-8}%)	15.43	0.62	75	0.75

At *p*H 7 the reduction of nitrobenzene at d.m.e. takes place in a 4-electron step. This is in conformity with the earlier investigations[9-11]. The αn_a values listed in Table 1 have been calculated at the surfactant concentration where maximum is just suppressed. Since 'n_a' has been shown[12] to be equal to 2, it becomes possible to estimate the

corresponding values of α. It is well known[13] that the presence of surfactants affects the kinetics of electrode processes and consequently αn_a (and hence α) values are also affected. Recently, Singh et al[14] while studying the suppression of Ni(II) maxima have compared the efficacies of the suppressors in terms of αn_a values at the concentrations where maximum is just suppressed. The order of αn_a values (which should also be the order of α-values) at any comparative situation for different surfactants should *signify the extent to* which the addition of ionic and non-ionic surfactants pushes the electrode reaction of nitrobenzene towards irreversibility. In the present study this push towards irreversibility at the point of just suppression is in the following order :

Cationic : LPC>CPC>CDBAC
Anionic : DSSS>SLS>DBS

Non-ionic : Gelatin>2-ethoxy ethanol>ethyldigol>Triton X-100. Thus CDBAC, DBS and Triton X-100 eliminate the polarographic maximum with least influence on the kinetics of electron transfer.

The effect of increasing concentration of the surfactants beyond the stage of just suppression on αn_a values has also been investigated and it has been observed that a decrease in the values of αn_a takes place. From this it is inferred[15-17] that the electrode reaction of nitrobenzene becomes more irreversible at higher concentrations of the surfactants.

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A Note on General Mathematical Expression for Stress-Strain Behaviour and Molecular Structure

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FROM statistical considerations, by a rigorous but straightforward mathematical treatment we obtained the following expression for the energy stored, $\Delta W^{(def)}$, due to deformation of a rubber-elastic polymer network at constant temperature T,

$$\begin{aligned}\Delta W^{(def)} = nkT[&(3/2)(L/nl)^2(\alpha_x^2+\alpha_y^2+\alpha_z^2-3)\\ &+(9/20)(L/nl)^4(\alpha_x^4+\alpha_y^4+\alpha_z^4-3)\\ &+(99/350)(L/nl)^6(\alpha_x^6+\alpha_y^6+\alpha_z^6-3)\\ &+\ldots] \qquad - KTln\,\alpha_x\alpha_y\alpha_z = \quad \ldots (1)\end{aligned}$$

For the last term of above equation, i.e., $KTln\,\alpha_x\alpha_y\alpha_z$ at present we assumed Flory's approach[1].

Where

n = number of effective flexible links in the polymer chain between adjacent crosslinks.

l = length of each flexible link.

k = Boltzmann constant.

T = absolute temperature.

L = average length per chain, in each of x, y and z directions.

and α_x, α_y and α_z are factors by which L is deformed in x, y and z directions. That is in x direction L changes to $L.\alpha_x$ in y direction to $L.\alpha_y$ and in z direction to $L\,\alpha_z$.

For elongation of a sample by a factor of L at constant volume[6,7] the tensile force, τ, per initial cross-sectional unit area as :

$$\tau=\frac{kT}{L^2l}\left[\alpha^{-1}\left(\frac{L\alpha}{nl}\right)-\alpha^{-\frac{3}{2}}\,\alpha^{-1}\left(\frac{L\alpha^{-\frac{1}{2}}}{nl}\right)\right] \quad \ldots (2)$$

or

$$\begin{aligned}\tau=(kT/L^2l)[&3(L/nl)(\alpha-1/\alpha^2)\\ &+(9/5)(L/nl)^3\left(\alpha^3-\frac{1}{\alpha^3}\right)\\ &+(297/175)(L/nl)^5\left(\alpha^5-\frac{1}{\alpha^4}\right)+\ldots] \quad \ldots (3)\end{aligned}$$

where α^{-1} denotes inverse Langevin function.

It is obvious that the first term of the right-hand

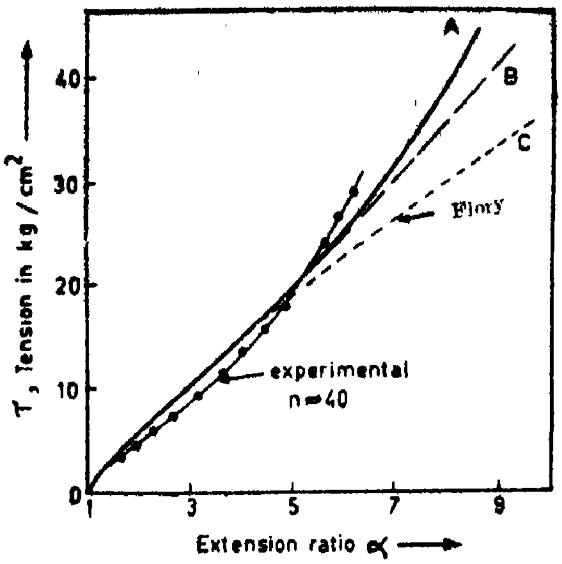


Fig. 1

side of above equation corresponds to Flory's equation and the first two terms together is similar to empirical equation of Mooney. But in our equation, unlike Mooneys, there is no unknown parameter. The curves from first (Curve C) approximation (Flory's) and from the second approximation (Curve B which is similar to Mooney's) have been compared with the curves from a typical experimental result[9,10] and the curve 'A' from our general equation (3). The theoretical curves are for $n=50$ and $T=300^\circ$K. The experimentnl curve is for $n=40$ and $T=300^\circ$K, approximately.

The theoretical results from Flory and others[3,4] (which came out as first approximation) and existing experimental results seem to support the new statistical approach to the theory of rubber elasticity.

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Colorimetric Determination of Organotrithiocarbonates and Mercaptans (via Trithiocarbonate Formation)

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ORGANOTRITHIOCARBONATES may be considered as salts of the corresponding trithiocarbonic acids(I) and are characterised

$$RS{-}\underset{\underset{S}{\|}}{C}{-}SH$$

(I)

by the presence of $-\overset{\overset{S}{\|}}{C}-S^-$ group. Inspite of the numerous valuable applications of organotrithiocarbonates in industry, medicine and agriculture, their estimation did not attract much attention. Verma and coworkers[1-5] have very recently developed various aqueous and non-aqueous redox methods for the determination of organotrithiocarbonates. In aqueous medium the methods were also extended to the determination of mercaptans after their quantitative transformation (with carbon disulphide and alkali) into organotrithiocarbonates.

$$RSH+CS_2+KOH \rightarrow RS{-}\underset{\underset{S}{\|}}{C}{-}SK+H_2O$$

Organotrithiocarbonates react with nickel(II) in slightly acidic medium to form brown coloured precipitates, which can be brought into solutions in the presence of acetone. The absorbance of the yellowish-brown coloured solution thus obtained can be measured photometrically. These observations have been exploited to develop a colorimetric method for the determination of small quantities of organotrithiocarbonates. The method has also been extended to the determination of mercaptans after their quantitative transformation into organotrithiocarbonates. The proposed methods are simple, accurate and reliable. The procedure is less time-consuming and may be used for routine analysis.

Experimental

Organotrithiocarbonates were prepared as described earlier[2]. The purity of the compounds was checked by non-aqueous redox titration[1]. The mercaptans (Fluka, Switzerland) were distilled twice before use. All other reagents used in this investigation were of guaranteed quality. Erma Photoelectric Colorimeter (Model A. E. 11), Japan was used for absorbance measurements.

* For correspondence

Determination of Organotrithiocarbonates: Acetone (4 ml) was added to a solution of nickel acetate (2 ml of 0.05N in water) and acetic acid (0.1 ml of 0.1N in water). Different aliquots of trithiocarbonate solution were then slowly added to it while stirring. After adding water (3 ml), the total volume of the mixture solution was made up to 10 ml with acetone. The absorbance of the yellowish-brown solution thus obtained was measured using 420 nm filter against a reagent blank. The results as calculated from the calibration data are given in Table 1.

TABLE 1.—COLORIMETRIC DETERMINATION OF ORGANOTRITHIOCARBONATES (TTC) AND MERCAPTANS

Compounds	Amount taken, mg	Amount found, mg	Error, %
Organotrithiocarbonates (potassium salts)			
Ethyl TTC	0.484	0.482	−0.41
	0.655	0.658	0.45
	0.886	0.882	−0.47
Isopropyl TTC	0.578	0.581	0.52
	0.770	0.766	−0.58
	0.962	0.962	0.00
n-Propyl TTC	0.942	0.937	−0.52
	1.167	1.162	−0.42
	1,885	1.878	−0.27
Isobutyl TTC	0.498	0.498	0.00
	0.783	0.781	−0.25
	1.399	1.403	0.29
n-Butyl TTC	0.232	0.231	−0.43
	0.580	0.582	0.34
	0.926	0.924	−0.21
n-Amyl TTC	0.456	0.453	−0.65
	0.647	0.645	−0.31
	1.124	1.127	0 26
Benzyl TTC	0.206	0.205	−0.48
	0.516	0.518	0.38
	1.032	1.028	−0.38
Mercaptans			
Ethyl mercaptan	0.127	0.128	0.78
	0.205	0.206	0.48
	0.280	0.278	−0.71
Isopropyl mercaptan	0.231	0.232	0.43
	0.308	0.306	−0.65
	0.385	0.385	0.00
n-Propyl mercaptan	0.214	0.213	−0.46
	0.324	0.325	0.31
	0.377	0.379	0.53
Isobutyl mercaptan	0.225	0.226	0.44
	0.286	0.286	0.00
	0.371	0.370	−0.24
n-Butyl mercaptan	0.157	0.158	0.63
	0.251	0.253	0.79
	0.314	0.316	0.63
n-Amyl mercaptan	0.184	0.183	−0.54
	0.273	0.275	0.73
	0.334	0.336	0.60
Benzyl mercaptan	0.162	0.161	−0.61
	0.324	0.322	—0.62
	0.583	0.585	0.34

Determination of Mercaptans: Different aliquots of solutions in acetonitrile of each mercaptan were taken. Each aliquot was treated with 0·5 ml of carbon disulphide and 2 ml of potassium hydroxide (app. 0.05N solution in water). The solution was neutralized with 0.1N acetic acid and transferred to a solution containing nickel acetate (2 ml) and acetic acid (0.1 ml). The volume of the solution was made up to 10 ml with acetone and the absorbance of the yellowish-brown solution thus obtained was measured using 420 nm filter against a reagent blank. The results as calculated from the calibration data are given in Table 1.

Results and Discussion

The results recorded in Table 1 show that the proposed method for the determination of organotrithiocarbonates gives accurate and reproducible results with a maximum error of 0.7%. The colour development of their nickel salts is instantaneous, and remains stable for about 10 minutes. This method is sensitive as well as precise. Sodium sulphide, urea, acetate, sulphate, carbonate and carbon disulphide do not cause any interference when present in small amounts. Xanthates, dithiocarbamates and amines, however, interfere.

The determination of mercaptans after their quantitative transformation (with carbon disulphide and potassium hydroxide) into the corresponding organotrithiocarbonates, excess of carbon disulphide does not cause any interference in the determinations which have been effected with a maximum error of 0.8%. Alcohols and amines (primary and secondary), however, interfere due to the expected formation of xanthates and dithiocarbamates respectively under the experimental conditions.

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Phytochemical Investigation on the Leaves of *Callicarpa macrophylla* Vahl.

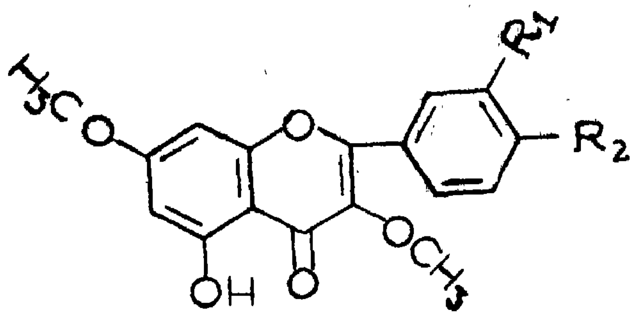
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PHYTOCHEMICAL investigation on the leaves of *Callicarpa macrophylla* Vahl. (Fam. Verbenaceae), led to the isolation of a number of terpenoids, sterols and some known flavonoids[1,2,3a,3b,3c]. The medicinal and piscicidal properties of this plant are well known[4,5,6a,6b,6c]. As a part of our programme on plants possessing antifeeding principles we became interested to reinvestigate the leaves of *Callicarpa macrophylla*. A flavone provisionally designated as CMF-1 has been isolated from the petrol ether extract of this plant along with ursolic acid and β-sitosterol. The characterisation of the flavone, CMF-1 is described in this communication.

The concentrated petroleum ether extract of the leaves of *C. macrophylla* on chromatographic resolution over silica gel and elution with benzene-ethylacetate (9.5 : 0.5) afforded a yellow solid which crystallised from petrol-benzene as pale yellow needles, m.p. 165-66°, $C_{18}H_{16}O_7$ (M^+ 344). A positive Shinoda test indicated it to be a flavone. Functional group analysis revealed the presence of three-OMe (one $6H$ singlet at 3.95δ and one $3H$ singlet at 4.0δ), an α, β-unsaturated ketone (ν_{max}^{KBr} 1660, 1600 cm^{-1}), a chelated phenolic $-OH$ (ν_{max}^{KBr} 3460 cm^{-1}, $1H$ singlet at 13.4δ, exchangeable with D_2O, brown colour with $FeCl_3$), a phenolic $-OH$ group ($1H$ singlet at 6.0δ, exchangeable with D_2O) and a complex aromatic substitution pattern (ν_{max}^{KBr} 1490, 1350, 1210, 1155, 810, 710 cm^{-1}). The presence of five aromatic protons is also discernible in the NMR spectrum. The substitution pattern of this compound is assignable from the NMR spectrum. In the NMR spectrum the quartet at 6.42δ (J = 3Hz) for $2H$ is due to the C_6 and C_8 protons[7]. The doublet at 7.04δ (J = 9 Hz) is assigned to the $C_{2'}$ and $C_{6'}$-protons[8]. An $1H$-multiplet at 7.68δ (J = 6 Hz) suggests the presence of $C_{5'}$-H in the compound. It appears, therefore, that the compound has got two substitutions in both A and B-rings respectively. No bathochromic shift of the longest wave length with $AlCl_3$ is a clear indication that there is one methoxyl group at C_3-position[9] [λ_{max}^{EtOH} 255, 357 nm, $\lambda_{max}^{EtOH+AlCl_3}$ 268, 360 nm] which is also in agreement with the mass spectral data[10] [m/e 329 (M-CH_3) and m/e 301 (M-$COCH_3$)]. The UV spectrum remained, however, unaffected in the presence of sodium acetate, indicating thereby that there is a $-OCH_3$ group[9] at C_7. Based on these evidence, the structure of the flavone may be written as (I) or (II), which is also consistent with the mass spectral fragmentation pattern. [m/e (M^+) 344, m/e 329 (M^+-15), m/e 301 (M^+-43), m/e 258, m/e 243, m/e 215, m/e 267 and m/e 105 (RDA fragments)].



I. $R_1 = OH$, $R_2 = OCH_3$
II. $R_1 = OCH_3$, $R_2 = OH$

A flavone having structure (II) has already been isolated from the plant *Larrea cauneifolia*[7] Cav. The UV and mass spectral data of (II) show close resemblance with the flavone, CMF-1 isolated by us. But we have observed certain differences in respect of the NMR signals of some protons and the UV shifts with $AlCl_3$ and NaOAc. However, a direct comparison of the properties (m.p., m.m.p., Co-TLC) of CMF-1 with those of the flavone (II)[7] was found to be similar, thereby proving the identity of CMF-1 as 5, 4'-dihydroxy 3, 7, 3'-trimethoxy flavone.

Experimental

M. p. is uncorrected, UV spectra were recorded in EtOH. For column chromatography silica gel (Gouri Chemicals, Calcutta, 60-100 mesh) was used. NMR spectrum was recorded in $CDCl_3$ with TMS as internal standard. The leaves of *C. macrophylla* were collected during the month of January, 1976.

Isolation

Air dried powdered leaves of *C. macrophylla* (1.5 kg) were exhaustively extracted (24 hr) with petroleum ether (60-80°) and the resulting extract was concentrated and chromatographed over silica gel (300 g). The chromatogram was eluted with solvents of increasing polarity. Benzene-ethyl acetate (1 : 1) eluates afforded a yellow oily residue which was further purified by rechromatography over silica gel. Elution of this chromatogram with benzeneethylacetate (9.5 : 0.5) furnished a yellow solid which crystallised from benzene-petrol as yellow needles, m.p. 165-66° (yield 0.002%) TLC : Rf. 0.7. (benzene-ethyl acetate-1 : 1), +ve Shinoda Test, +Ve $FeCl_3$ color reactions.

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OBITUARY



PROFESSOR H. N. KHASTGIR

Professor H. N. Khastgir passed away in Calcutta on May 31, 1978 after a coronary attack when he was only 54.

Prof. Khastgir was born on December 3, 1923 at Chittagong, now in Bangladesh. He passed the Matriculation Examination in the First Division with a scholarship from Bengal Academy High School, Rangoon, Burma in 1940. During the Second World War he left Burma with his parents and other members of his family in the last boat leaving Rangoon before the Japanese occupation. In 1942 he passed the I. Sc. Examination in First Division from Rangoon University organised by the evacuee Government of Burma at Lucknow. He passed the B.Sc. Examination from Vidyasagar College, Calcutta in 1944 with honours in Chemistry and passed the M.Sc. Examination from the University of Calcutta in 1946 in Chemistry with Organic Chemistry as his special subject.

Prof. Khastgir joined the City College, Calcutta as a Lecturer in Chemistry in 1947 and started his research work under Prof. D. K. Banerjee as a part time research worker. He received his Ph.D. (Sc.) degree from the University of Calcutta in 1952 working on different routes towards the total synthesis of steroids. From 1952 to 1954 Prof. Khastgir worked as a Post-doctoral Research Fellow under Prof. Carl Djerassi at Wayne State University, Detroit, Michigan, U.S.A.. Here he worked on the structure of several natural products. From 1954 to 1955 he worked under Prof. Gilbert Stork as a Post-doctoral Fellow at Columbia University, New York, U.S.A. and carried out researches on the total synthesis of steroids. In 1955 he returned to India and joined East India Pharmaceutical Works Ltd., Calcutta as a Research Officer. Here he worked on the structure of nimbin, nimbiol, psoralidin, multiflorenol, etc. He also developed a cheap method for the conversion of diosgenin into progesterone.

In 1962 Prof. Khastgir joined the Glaxo Research Laboratories, Bombay and stayed there for a short period. He joined the newly started University of North Bengal during the last part of 1962 as Reader and the first Head of the Department of Chemistry. He was responsible for the planning of teaching programmes in Chemistry leading to B.Sc. and M.Sc. degrees. He also organised research work in different branches in Chemistry and it is only due to him that the Department of Chemistry of the University of North Bengal is considered as one of the foremost research centres in Organic Chemistry. He became the Professor and Head of the Department of Chemistry at the same University in 1968. Due to his poor health he however relinquished his duties as Head of the Department in 1976 and served merely as Professor of Chemistry which post he held until his untimely death.

Prof. Khastgir made significant contributions in various fields of Organic Chemistry. But his contribution in the field of triterpenoids is specially outstanding. In fact no text book on triterpenoids can be written without significant references to Prof. Khastgir's research work. Prof. Khastgir published 77 papers and there are some more yet to be published. Altogether 8 students have received Ph.D. (Sc.) degree working under his guidance. In 1971 Prof. Khastgir visited Hungary under the Cultural Exchange Programme. The Scientific Community of India has suffered a serious loss in the sad and untimely demise of Prof. H. N. Khastgir.

P. Sengupta